

## Chapter 7

# One Hundred Volatile Years of Volcanic Gas Studies at the Hawaiian Volcano Observatory

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The smell of sulphur is strong, but not unpleasant to a sinner.

—Mark Twain, *Letters from Hawaii*, 1866

### Abstract

The first volcanic gas studies in Hawai‘i, beginning in 1912, established that volatile emissions from Kīlauea Volcano contained mostly water vapor, in addition to carbon dioxide and sulfur dioxide. This straightforward discovery overturned a popular volatile theory of the day and, in the same action, helped affirm Thomas A. Jaggar, Jr.’s, vision of the Hawaiian Volcano Observatory (HVO) as a preeminent place to study volcanic processes. Decades later, the environmental movement produced a watershed of quantitative analytical tools that, after being tested at Kīlauea, became part of the regular monitoring effort at HVO. The resulting volatile emission and fumarole chemistry datasets are some of the most extensive on the planet. These data indicate that magma from the mantle enters the shallow magmatic system of Kīlauea sufficiently oversaturated in CO<sub>2</sub> to produce turbulent flow. Passive degassing at Kīlauea’s summit that occurred from 1983 through 2007 yielded CO<sub>2</sub>-depleted, but SO<sub>2</sub>- and H<sub>2</sub>O-rich, rift eruptive gases. Beginning with the 2008 summit eruption, magma reaching the East Rift Zone eruption site became depleted of much of its volatile content at the summit eruptive vent before transport to Pu‘u ‘Ō‘ō. The volatile emissions of Hawaiian volcanoes are halogen-poor, relative to those of other basaltic systems. Information gained regarding intrinsic gas solubilities at Kīlauea and Mauna Loa, as well as the pressure-controlled nature of gas release, have provided useful tools for tracking eruptive activity. Regular CO<sub>2</sub>-emission-rate measurements at

Kīlauea’s summit, together with surface-deformation and other data, detected an increase in deep magma supply more than a year before a corresponding surge in effusive activity. Correspondingly, HVO routinely uses SO<sub>2</sub> emissions to study shallow eruptive processes and effusion rates. HVO gas studies and Kīlauea’s long-running East Rift Zone eruption also demonstrate that volatile emissions can be a substantial volcanic hazard in Hawai‘i. From its humble beginning, trying to determine the chemical composition of volcanic gases over a century ago, HVO has evolved to routinely use real-time gas chemistry to track eruptive processes, as well as hazards.

### Introduction

Volcanic gases are a dominating force in eruptive activity. Although the thermal and density contrasts between magma in a volcanic system and the surrounding country rock result in the rise of melt from depth to the edifice, the exsolution, expansion, rise, and separation of volatiles are what drive both effusive and explosive eruptions.

Thomas A. Jaggar, Jr., founder of the Hawaiian Volcano Observatory (HVO), stated it well: “The observatory worker who has lived a quarter of a century with Hawaiian lavas frothing in action, cannot fail to realize that gas chemistry is the heart of the volcano magma problem” (Jaggar, 1940). Despite the fervor of this statement, hazardous field conditions associated with the sampling of volcanic vents and the early evolutionary state of analytical techniques applied to gas samples conspired to produce only modest progress in the understanding of gas release processes by 1940, when Jaggar opined the above remark.

In this chapter, we trace the progress made at HVO in understanding the role of volatile emissions in volcanic processes. Gas studies at HVO evolved episodically, not unlike the eruptive activity that researchers were tracking. In the early days, gas studies relied on volcanic action to provide

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sampling opportunities, as well as the often fitful progression of technology, to provide the tools to study volcanism. Because of the infrequency of sustained eruptions on Mauna Loa and the comparative difficulty of working there, gas studies techniques and progress have generally evolved on Kīlauea and then been applied to the larger mountain. Paul Greenland reviewed the major research on eruptive gases leading up to HVO's 75th anniversary (Greenland, 1987a). In recognition of HVO's centennial and, owing to the obscurity of some of the earlier documentation, here we emphasize the formative years of gas studies, as well as those years postdating Greenland's (1987a) review.

HVO gas studies, to date, can be reasonably grouped in three distinct epochs of progress, each of which produced milestones that helped advance the science. At HVO's inception, Halema'uma'u lava lake within Kīlauea's summit caldera provided an excellent environment to observe volcanic gas release first hand. As with so much of the progress achieved by all the disciplines at HVO, close proximity to eruptive activity—literally, right out the back door—and the relative passivity of that activity helped workers make considerable progress within a comparatively short time. This first epoch saw development of the rudiments of gas sampling and analysis, and, although the extreme temperatures and the corrosiveness of the gases were challenging, the first data from these experiments revealed the fundamental ternary chemical makeup of volcanic gas emissions.

Opportunities to study eruptive gases at Kīlauea ceased as magma withdrew from the summit in 1924, and eruptive activity was subdued or absent for nearly 40 years. During the gap, the second epoch of growth in knowledge about volcanic gases occurred, owing to demand-driven improvements in analytical technology. These improvements fueled advances in the ability to sample and analyze gases when vigorous eruptive activity returned to the summit in the 1960s.

Beginning in 2000, a sea change occurred in the way HVO monitored eruptive activity, caused by a major increase in computing and networking capability and especially in the centralization of data and capability to visualize it in near-real time. These improvements made it easier than ever before to track geophysical and geochemical data streams contemporaneously during the course of Kīlauea's long-running (1983–present) East Rift Zone eruption. This rich, real-time analytical environment, in combination with an upwelling of new gas-measurement techniques, provided opportunities to test theories about magma movement during a surge in Kīlauea's magma supply. Major changes in eruptive activity both at Kīlauea's summit and along the East Rift Zone provided the crucial data needed to further test and extend previously constructed models. The persistent high level of eruptive activity during this third epoch, along with the watershed of gas-studies tools and techniques, also occasioned a better appreciation of volatiles as a volcanic hazard requiring assessment, response, and mitigation, rather than something that could be ignored or downplayed in comparison with other, more visible volcanic processes.

## Early and Middle Years, 1912–50s: Gas-Sampling Methods and the Ternary Compositional Basics

At the time of HVO's founding, several workers had already written about Kīlauea's volatile emissions. In his book "Vestiges of the Molten Globe, Part II," William Lothian Green, a self-taught volcano scientist-observer and longtime resident of Hawai'i, hypothesized that water was not a fundamental component of Hawaiian volcanic gas emissions (Green, 1887; Day and Shepherd, 1913). Although Green did not actually collect or analyze gas samples in the conventional sense, he was a careful observer; amongst his many interpretations of Kīlauea and Mauna Loa plume clouds, he attributed the visible fume above eruptive vents and the Halema'uma'u lava lake as simply a convective interaction between the tremendous heat given off by molten lava and the moisture laden trade winds passing over eruptive sources. Years later, Albert Brun, a Swiss chemist who made actual field measurements of volcanic gas emanations on Kīlauea and other volcanoes, put forth a similar conclusion (Brun, 1913). Reginald Daly, a professor at Harvard who visited Kīlauea in 1909, was more open-minded on the issue of water as a volcanic gas. While acknowledging the conclusions of Green and Brun about Kīlauea, Daly believed that volatiles, possibly including water, played an important role in volcanism (Daly, 1911).

The writings of Green, Brun, and Daly formed the knowledge base that fueled the interest and experimental plans of A.L. Day and E.S. Shepherd of the Carnegie Institute's Geophysical Laboratory, the first two investigators to make gas measurements at Kīlauea under the HVO banner. The water question was a popular topic of the day, but Day and Shepherd had accepted Brun's conclusion that Kīlauea's volatile emissions were anhydrous and planned their experiments accordingly.

Day and Shepherd's gas collection scheme consisted of a series of 20 half-liter flasks strung together serially (Day and Shepherd, 1913). One end of this sampling string was connected to a glass-lined iron sampling pipe, where the gas would enter the string; the other end was linked to a hand-operated piston pump, used to draw gas through the string of flasks.

Shepherd had spent the second half of 1911 working at Kīlauea alongside Frank Perret, conducting observations at the Halema'uma'u lava lake and assisting in the first in situ lava temperature measurements. This experience served him well when he returned to the volcano with A.L. Day the following year. On May 28, 1912, Day and Shepherd had the good fortune of happening upon a volcanic gas sampler's dream vent. On the floor of Halema'uma'u, a pressurized opening in what might be best described as a hornito vented burning gas to the air, offering an opportunity to sample essentially pristine volatile emissions. These conditions were exactly what the two researchers had been hoping for (fig. 1). They set up



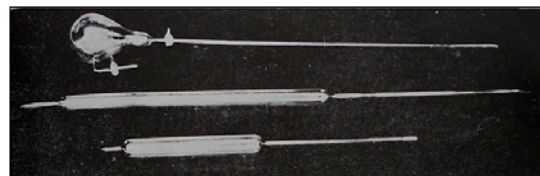
**Figure 1.** E.S. Shepherd (left) and F.B. Dodge sample pristine eruptive gases at Halema'uma'u Crater, May 28, 1912. Dome-shaped hornito just right of center accommodated a 0.3-m-long iron sampling pipe that was linked through glass tubing to 20 serially connected sampling bottles contained within the crate between the two men and, finally, to a hand-operated pump.

their collection gear, placed the end of a sampling tube within the hornito just past the burning gas jet, and began to pump. Because of Brun's earlier conclusion, Shepherd and Day made no provision to collect condensed moisture, because they expected no water.

What happened next surprised them. Large amounts of fluid, later determined to be water, began to condense in their apparatus under ambient temperature conditions. Within 15 minutes, they had collected 300 mL of this aqueous condensate, along with a substantial volume of noncondensable "dry" gas. Most of the condensation occurred in the first few flasks of the sampling string because of the large temperature contrast between the hot vent and the relatively cool first flasks in the string. Thus, instead of having 20 replicate samples of a single composition to analyze, thereby ensuring high-precision results, Day and Shepherd obtained 20 bottles with varying amounts of volatile constituents scattered among them.

Although their experimental plan did not anticipate water, Day and Shepherd made the best of it. Partial analyses carried out 4 days later at the College of Hawai'i on O'ahu confirmed the presence of  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{CO}$ , along with the water and dissolved gases composing the condensate. Because of the high water solubility of  $\text{SO}_2$  and haloacids, the O'ahu analyses were partial and preliminary. The rest of the samples were taken back to the Carnegie Institute's Geophysical Laboratory in Washington, D.C., for detailed analysis of both the dry gas and the remaining aqueous condensate.

Day and Shepherd's May 28, 1912, samples affirmed not only that water was part of the makeup of pristine volcanic gases but also that it was a principal component, along with  $\text{CO}_2$  and  $\text{SO}_2$ . Thus, in spite of their compromised gas-collection apparatus, they readily characterized the volatile



**Figure 2.** Early 1900s vacuum-type gas-sampling bottles. More fragile lower and middle bottles are from Shepherd, Day, and Jaggar era, circa 1912–25. Elongate, thin glass bulb at right end of each bottle was melted or broken to admit gas when placed inside a hot vent, attached to end of a 3-m-long pole, then carefully resealed by melting after gas was sampled. Top bottle, by Stanley Ballard of the University of Hawai'i, circa 1938, improved on earlier ones by being sturdier, with a tip that was broken open for sampling using an attached wire. This newest bottle was resealed after sampling by closing stopcock at base of bulb.

emissions at Kilauea as a ternary mixture ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{SO}_2$ ) with minor amounts of other species, including  $\text{CO}$  and  $\text{H}_2$ . The copious amount of water in the May 28 samples propelled Day and Shepherd to develop an alternative gas-collection strategy because of the large, but incomplete, dissolution of acidic gases, like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{HCl}$ , and  $\text{HF}$ , in the condensate fraction. The alternative approach sought to draw the gases, including water, into a newly designed, evacuated sampling bulb (fig. 2). Although Day and Shepherd recognized water as a substantial component of volcanic exhalations, they had yet to establish the source mechanism for the presence of water, and water's importance in the physicochemical equilibrium of magma.

A.L. Day returned to the Carnegie Institute's Geophysical Laboratory to resume his post as its director, but E.S. Shepherd kept a close collegial relationship with HVO, returning to refine gas-sampling methods and to work with Jaggar in order to make this technology part of the fabric of HVO's research. Thus, gas studies became another research tool at HVO for understanding volcanic processes.

Shepherd and Jaggar watched for gas-sampling opportunities, and together they published 26 variously partial and full sets of analyses for gas samples collected during 1912–19 (fig. 3; Shepherd, 1921, 1925; Jaggar, 1940), the bulk of which came from a systematic sampling campaign carried out by Jaggar in 1918 and 1919. Jaggar, in consultation with Shepherd, endeavored to obtain samples uncontaminated by atmospheric oxygen, and a subset of these samples was used many years later to infer Kilauea's magmatic source conditions (Matsuo, 1962; Nordlie, 1971; Gerlach, 1980).

Shepherd and Jaggar's sampling focus was on what Shepherd called "volcano gases," or what we would today



call eruptive gases. Shepherd also acknowledged the potential value of studying fumarolic solfatara gases, although he saw these gases, as well as those from wells, springs, and mines, as a less straightforward path toward understanding volcanic plumbing and processes. Shepherd, back at the Geophysical Laboratory, was also interested in the gases released by rocks heated in a vacuum, seeing these products as the last stop in the gas-release process (Shepherd, 1925).

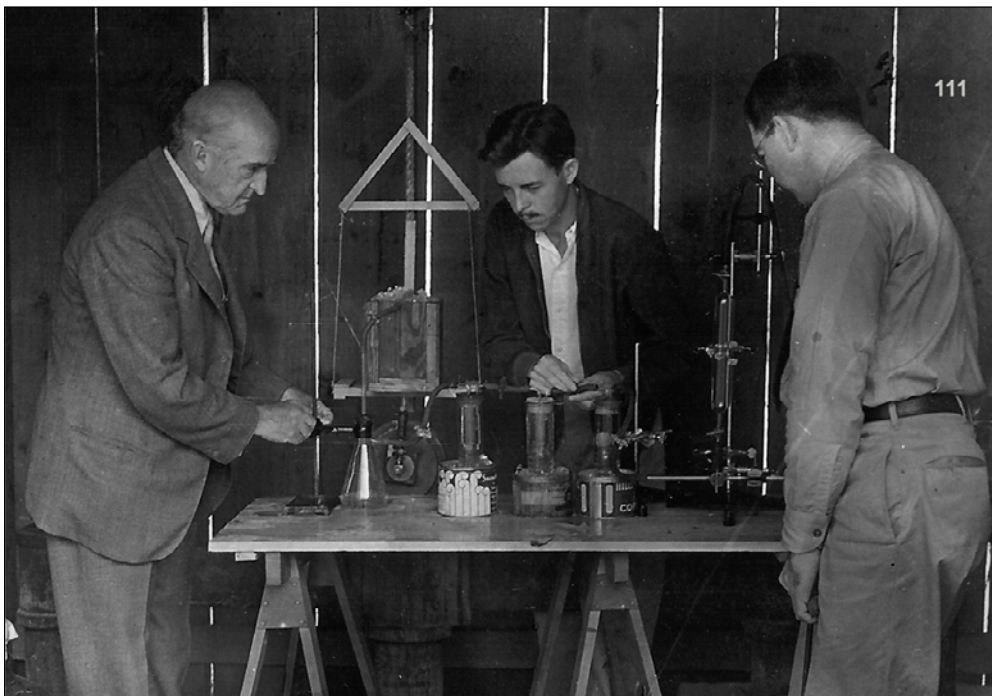
The withdrawal of magma from beneath Halema'uma'u that preceded the explosive 1924 eruption effectively began a hiatus in eruptive-gas sampling at Kīlauea that lasted nearly four decades. Shepherd and Jaggar used the interval to carefully consider the implications of the data they had collected (Shepherd, 1925, 1938; Jaggar, 1940). With the lapse in eruptive-gas sampling, Jaggar adjourned with colleagues S.S. Ballard and J.H. Payne of the University of Hawai'i, who were collecting and studying gases from a 21-m-deep well located at Sulphur Banks, on the north edge of Kīlauea Caldera (fig. 4). Ballard and Payne

were interested, among other things, in improving methods for collecting and analyzing volcanic gases. At Sulphur Banks, they took advantage of the site as a long-lived gas-emitting feature and established the first multiyear gas sampling program there (Ballard and Payne, 1940). At this site, they reported an "incident" of increased  $H_2S$  emission before the 1940 Mauna Loa eruption (Payne and Ballard, 1940). This inferred link between Sulphur Banks gas release and Mauna Loa eruptive activity, though unsubstantiated mechanistically and never observed again, was the first suggestion of eruptive-gas precursors in the Kīlauea literature.

Thomas A. Jaggar, Jr., retired in 1940 after publishing his paper "Magmatic Gases" in the *American Journal of Science*, where he challenged future volcanologists to consider a list of working hypotheses regarding volcanic gas studies (Jaggar, 1940). Shepherd's, Jaggar's, Ballard's, and Payne's diligence notwithstanding, the available analytical techniques of the day were stretched to the limits of detection, pursuant to quantifying



**Figure 3.** A. Lancaster (left) and E.S. Shepherd sample gases at Halema'uma'u in 1917. The tip of an evacuated tube gas-sampling bottle, wired to the end of a bamboo pole, was inserted through a small, flaming hole in the lava-lake crust. The soft glass window at the tip of the bottle melted, allowing magmatic gas to be sucked inside. Once filled, the bottle was resealed by folding the melted tip against a hot lava surface.



**Figure 4.** From left to right, T.A. Jaggar, Jr., J.H. Payne, and S.S. Ballard sample gas from a 21-m-deep geothermal well located at North Sulphur Banks (on north rim of Kīlauea Caldera) circa 1937. Ballard operates a hand pump at lower right, drawing gas from circular wellhead (apparent between Jaggar and Payne) through a hidden, ice-chilled flowthrough bottle and then through a flask and series of wash bottles containing KOH solution to remove acidic gases and water. Final "dry" gas collected in vertical flowthrough bottle is located middle right of frame between Payne and Ballard.

the chemical constituents in the samples obtained. Further advances in sampling and analytical technology would be needed if volcanic gas studies were to move forward.

## Technological Renaissance and Eruptive Reawakening Fuel Progress in Gas Studies: The 1960s Through the 1990s

Much of the U.S.'s focus had been on national-security issues related to World War II and the Korean War rather than on volcanoes during the years that followed the Halema'uma'u eruptive shutdown. This emphasis on national defense, however, led to advances in analytical and computational technology throughout the 1950s and 1960s, the benefits of which spanned civilian, as well as military, applications. For example, the Clean Water Act of 1960, the Clean Air Act of 1970, and the establishment of the Environmental Protection Agency and the Occupational Safety and Health Administration in 1970 created widespread regulatory needs for rapid and accurate analytical methods to study water and gas samples (albeit not volcanic ones). Gas chromatography (GC), chemically selective electrode methodology, and analytical spectroscopy developed rapidly, in part to meet the growing environmental requirements. These technologies also helped scientists drastically improve detection limits and accuracy for analyzing the principal constituents of volcanic gases.

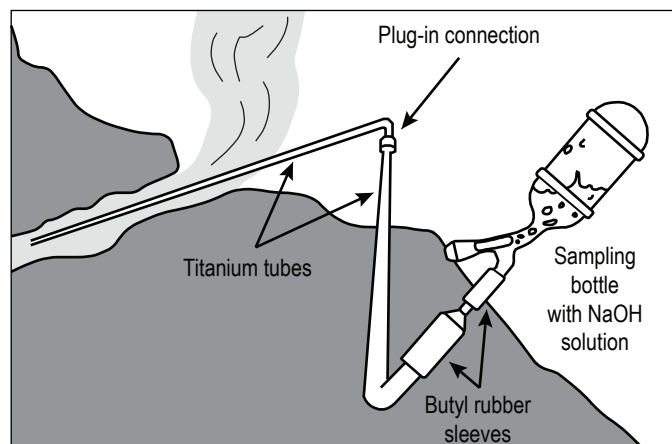
### Assembling New Tools to Study Gas Release

One example of the leveraging of environmental-science capabilities was when Werner F. Giggenbach, a gas-studies worker in New Zealand, developed an innovative method to sample and analyze volcanic and geothermal gases, which revolutionized volcanic gas studies worldwide, as well as at HVO (Giggenbach, 1975). His innovation relied on the fact that volcanic emissions are composed chiefly of water vapor and the so-called acid gases, including  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ , and  $\text{HF}$ . For most volcanic and geothermal systems, these species compose more than 95 percent of the emitted volatiles, and all of them are highly soluble in caustic (basic) solution.

As with other investigators studying volcanic emissions, Giggenbach wanted a complete gas analysis, including the non-acidic gases. Thus, he partially filled his collection flasks with caustic  $\text{NaOH}$  solution and then evacuated the headspace of the flask. A sampling tube, usually of an inert material, such as aluminum oxide ceramic or corrosion-resistant titanium, brought hot volcanic gas to the inverted flask, which, when opened, caused the acidic gases to be stripped out by the  $\text{NaOH}$  solution as they were drawn into the bottle (fig. 5; Giggenbach, 1975). The non-acidic gases, including  $\text{H}_2$ ,  $\text{He}$ ,  $\text{CO}$ , and any unreactive atmospheric constituents, such

as  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{Ar}$ , passed unaffected through the solution and accumulated in the headspace. These headspace gases were analyzed by the newly available GC technique, and the acidic gases were determined by wet chemistry methods, ion-selective electrodes, and gravimetric analysis. This novel approach to sample collection put complete gas analysis within the reach of any researcher with access to a relatively modest GC, an analytical balance, a pH meter and electrodes, a manometer, and standard wet chemical supplies. This powerful new analytical technique rapidly became popular, and Kīlauea proved itself an excellent place to apply it for studying volcanic gases.

Another major gas-studies advance at HVO that was brought on by the rapid expansion of the environmental-science field was adoption of the correlation spectrometer, or COSPEC, an instrument that became commercially available in the mid-1960s to measure the pollution released by power plants and other industrial smokestacks (Moffat and Millan, 1971). The remote capability of the technique was a remarkable aspect. The COSPEC, pointed at a gas-bearing plume, measures the proportion of scattered ultraviolet sunlight energy absorbed by  $\text{SO}_2$ . The first volcanic COSPEC measurements were obtained in Japan at Mount Mihara in 1971 (Okita, 1971). Richard Stoiber and research colleagues from Dartmouth College began experimenting with the COSPEC at Kīlauea in 1975 (Stoiber and Malone, 1975). During these early trials, they demonstrated that the  $\text{SO}_2$  emission rate could be measured by driving the vehicle-mounted, upward-looking instrument along the road beneath Kīlauea's passive summit plume. The product of the concentration-pathlength cross section, recorded on a paper strip chart recorder, and the wind velocity yielded the  $\text{SO}_2$



**Figure 5.** W.F. Giggenbach's volcanic-gas-sampling technique, illustrated here, relied on mechanically durable, chemically resistant titanium tubing to bring magmatic gas to an evacuated sampling bottle partially filled with  $\text{NaOH}$  solution. The inverted bottle is opened, allowing gas to bubble through solution. Acidic gases ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ ) and  $\text{H}_2\text{O}$  dissolve in the  $\text{NaOH}$  solution, and insoluble gases ( $\text{H}_2$ ,  $\text{He}$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ ) pass through, and accumulate in, the headspace.

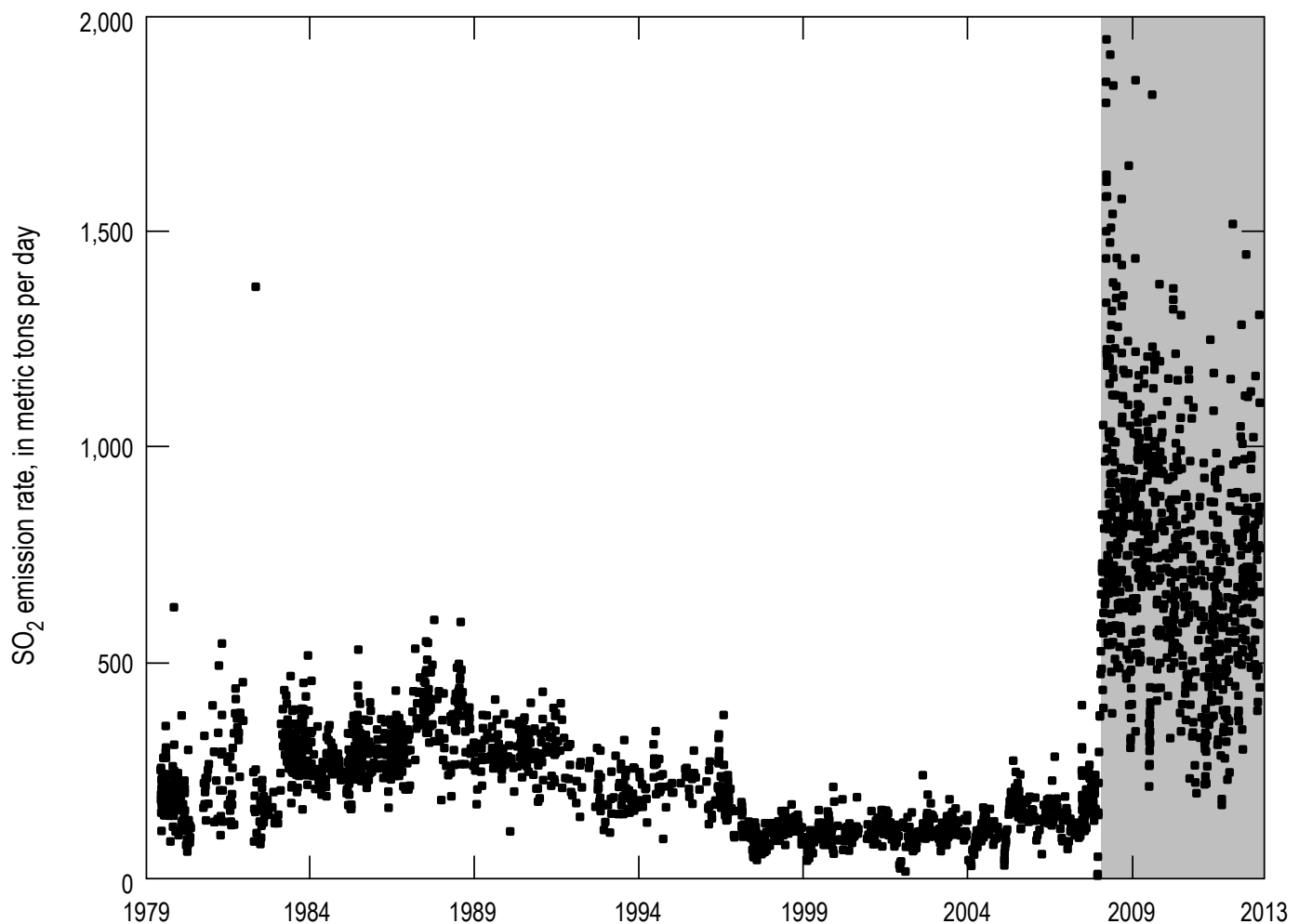
emission rate. Although the technique was novel, conversion of the chart-recorder trace to a concentration cross-sectional area and calculation of an  $\text{SO}_2$  emission rate were laborious multihour tasks.

The measurements by Stoiber and follow-on colleagues indicated that Kīlauea, even when not actively erupting, emitted as much as several hundred tons of  $\text{SO}_2$  each day—an amount equivalent to that of a small coal-fired powerplant (Stoiber and Malone, 1975). The COSPEC technique showed enough promise that regular measurement of  $\text{SO}_2$  emission rates became part of HVO's routine monitoring by 1979 (fig. 6). A favorable attribute of routine, campaign-style COSPEC measurements was building, for the first time, a volatile-emission time series that could be compared to

contemporaneous geophysical data. One of the first such investigations, for example, examined the relation between Kīlauea's daily  $\text{SO}_2$  emission rate, caldera seismicity, and fortnightly Earth tides (Conner and others, 1988).

### HVO Commits Full-Time Staff to Volcanic Gas Studies

In 1978, Tom Casadevall joined the HVO research staff, inaugurating a permanent commitment by HVO to volcanic gas studies, with laboratory technical expertise from Bruce Furukawa, a University of Hawai'i chemistry department graduate with a strong electronics background. In addition



**Figure 6.**  $\text{SO}_2$  emission rates from Kīlauea's summit caldera became part of the regular monitoring program at HVO in 1979. Measurements made by vehicle-based COSPEC revealed fitful degassing during runup to 1983 East Rift Zone eruption. The first 10 years of that eruption saw increased throughput of summit magma-storage complex and resulted in a general doubling of emissions before declining somewhat. The next large increase began in late in 2007 and continued through onset of 2008 summit eruption. Although this eruption began officially in March 2008, increased emissions had already forced long-term closure of the downwind part of Crater Rim Drive in the previous month. In this plot, each data point represents an average of several transects of the plume. Error bars are omitted for clarity, but uncertainty is generally within 30 percent of the measured value through 2007. Values shown beginning in early 2008 (shaded region) represent minimum constraint, possibly underestimating actual emission rates by factor of 2 to 5 (Elias and Sutton, 2012).



to establishing routine  $\text{SO}_2$  emission-rate measurements, Casadevall, along with Rick Hazlett of the University of Southern California, conducted the first detailed inventory of significant thermal features on Kīlauea and Mauna Loa volcanoes (Casadevall and Hazlett, 1983). Paul Greenland, an analytical geochemist who had worked for many years at the U.S. Geological Survey's National Center in Reston, Va., joined HVO in 1980. Greenland immediately set to work building the first gas-analysis capability at the Observatory and began systematically characterizing the volatile species chemistry of Kīlauea's many steam vents and solfataras.

In addition to mapping thermal features and initiating the use of the COSPEC on Kīlauea and Mauna Loa, Casadevall and Furukawa helped advance a new type of volcanic gas study: continuous, in situ, sensor-based monitoring. The electrochemical gas sensors used in this pursuit were another technology that HVO and its adjuncts adapted from the environmental movement. These sensors produce an electrical output proportional to the abundance of a specific gas species present in their immediate environment. A harsh volcanic setting like Kīlauea, however, presents analytical challenges to most commercially available sensors.

Motoaki Sato, of the USGS in Reston, Va., had pioneered the adaptation of in situ chemical-sensing methodology on Kīlauea beginning in 1966, when he and Thomas Wright made the first field measurements of oxygen fugacity ( $f_{\text{O}_2}$ ) on the surface of a newly emplaced lava lake at Makaōpuhi Crater (Sato and Wright, 1966). They chose to study  $f_{\text{O}_2}$  because of the importance of this intrinsic parameter to magmatic differentiation (Sato and Wright, 1966; Sato, 1978). Other gas-forming elements, such as carbon, hydrogen, and sulfur, react with oxygen and with mineral assemblages, changing the relative oxidation state of the melt during these interactions and during exsolution. Sato and Wright (1966) insisted that a better understanding of the amounts and types of these species could reasonably lead to a more thorough comprehension of magmatic differentiation as a part of the eruptive process.

One specific outcome of Sato and Wright's Kīlauea  $f_{\text{O}_2}$  study was their recognition of the importance of molecular hydrogen ( $\text{H}_2$ ) in influencing the oxidation state of basaltic magma. Accordingly, Sato went on to develop a robust, field deployable  $\text{H}_2$  and reducing-gas sensor based on fuel-cell technology (Sato and McGee, 1981; Sato and others, 1986). A network of gas-monitoring sites with  $\text{H}_2$ /reducing-gas sensors was established on Kīlauea, and a single site was installed on Mauna Loa. The Kīlauea network used a hybrid communications technology to make data available rapidly. An analog radio-telemetry system sent signals back to HVO for real-time display, and, simultaneously, the data were transmitted by way of geostationary satellite to Wallops Island, Va., where Sato's group could access the data in near-real time (McGee and others, 1987).

Casadevall's, Greenland's, and Furukawa's initiation of regular  $\text{SO}_2$ -emission-rate measurements and their pursuit of detailed fumarole gas chemistry greatly improved HVO's

capability to ask and answer fundamental questions related to gas release, further enhancing understanding of volcanic processes. In addition, the network of continuous, near-real-time gas sensors honed the emission-rate and chemical data to a fine temporal edge.

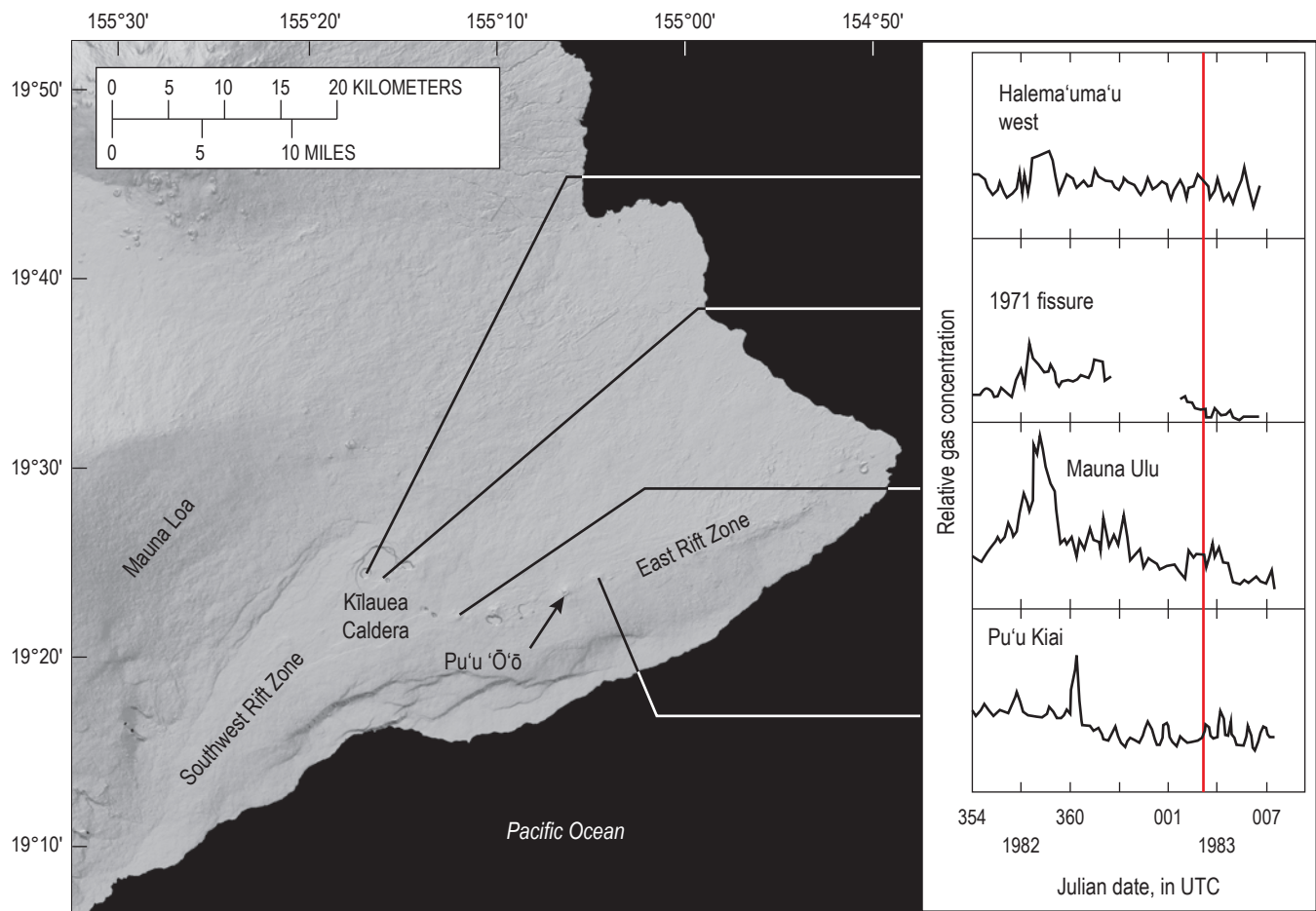
## Kīlauea's Renewed Restlessness Tests Volcanic Gas Studies' Mettle While Researchers Synthesize a Volatile-Release Model

The growth and alignment of volcanic-gas-studies capabilities at HVO came just in time for an eruptive reawakening at Kīlauea. A near-surface intrusion on Kīlauea's Southwest Rift Zone in 1980 and two one-day summit eruptions in 1982 helped stimulate investigation of the chemistry of directly sampled eruptive gases in the newly configured HVO laboratory (Greenland, 1987a). Increases in  $\text{SO}_2$  emission rates were measured by COSPEC during a 1979 upper East Rift Zone eruption, a 1980 upper East Rift Zone intrusion, and the April 1982 summit eruption (fig. 6). These events were all short lived and occurred with little warning, further demonstrating the importance of a permanent volcanic-gas-studies presence at HVO.

This point was underscored in late 1982 when the continuous gas-monitoring network established by Sato's group captured a widespread gas-release sequence that began at Kīlauea's summit in the last days of December and, over the course of 3 days, propagated with the eruptive dike nearly 30 km down the East Rift Zone before the January 3 onset of what became known as the Pu'u 'Ō'ō-Kupaianaha eruption (fig. 7; McGee and others, 1987). Continuous monitoring of helium at Sulphur Banks showed a simultaneous decrease in gas release during this interval (Friedman and Reimer, 1987). Friedman and Reimer, however, did not suggest a cause for the decrease, which could reasonably have been associated with a pressure decrease and closure of caldera ring faults as magma left the summit region to feed the impending East Rift Zone eruption.

The early years of the Pu'u 'Ō'ō-Kupaianaha eruption provided numerous opportunities for HVO and adjunct researchers to use the new analytical methods to expand and test models for how Kīlauea and similar volcanoes work. Initial gas samples from the East Rift Zone eruption showed a uniformly  $\text{CO}_2$ -depleted condition that Greenland (1984) attributed to preeruptive magma storage in a shallow reservoir. Using the detailed chemistry of vent-gas samples and the first airborne  $\text{CO}_2$  and  $\text{SO}_2$  emission-rate measurements at Kīlauea's summit and East Rift Zone, he refined this interpretation specifically to apply to magma storage beneath the volcano's summit (Greenland and others, 1985).

Terry Gerlach, who joined the USGS Volcano Hazards Program in 1991, was also keenly interested in Kīlauea's eruptive gases. At the onset of the Pu'u 'Ō'ō-Kupaianaha



**Figure 7.** Continuous monitoring at Kilauea in late December 1982 captured preeruptive gas release that began in summit area and spread down East Rift Zone. In all, 6 reducing-gas sensors at 5 sites (4 plots shown here), stretching 30 km across volcano, recorded event over course of 3 days and relayed collected data in near-real time by geostationary satellite. Pu'u 'Ō'ō eruption began January 3, 1983 (red line). Adapted from McGee and others, 1987.

eruption, Gerlach, while still at Sandia National Laboratories, had become the latest researcher to reinterpret the famous Jaggard gas collections of 1917–19 from a thermodynamic perspective, identifying contamination by meteoric water as a principal cause of their apparent disequilibrium (table 1; Gerlach, 1980).

When episodic high lava fountaining began at the East Rift Zone in 1983, Gerlach and colleague Ed Graeber, in consultation with HVO researchers, sampled the eruptive vents and analyzed the gases as Greenland had done. In their landmark paper in the journal *Nature*, Gerlach and Graeber (1985) began by considering the parental volatiles trapped in olivine crystals deep beneath Kilauea; then, progressively, they followed the degassing process by examining the volatile content of samples quenched at the somewhat-lower pressures of the submarine seafloor. Finally, they studied the volatiles remaining in subaerial eruptive spatter degassed to atmospheric pressure. These data, along with their careful analyses of gases collected close to where Pu'u 'Ō'ō formed,

and in HVO's SO<sub>2</sub> emission- and eruption-rate records, helped them construct a comprehensive volatile budget for Kilauea Volcano spanning 27 years of intermittent activity (tables 2, 3; Gerlach and Graeber, 1985).

For their model of gas release at Kilauea, Gerlach and Graeber (1985) identified two principle eruptive-gas types representing compositional end members. For a concerted, single-stage summit eruption, they proposed that as magma ascends directly to the surface, it erupts and degasses in a single stage and releases a CO<sub>2</sub>-rich "Type I" gas (fig. 8A). This eruptive configuration prevailed throughout Kilauea's continuous 19th-century Halema'uma'u lava-lake activity, which lasted until 1924. This interval also produced Jaggard and Shepherd's classic gas collections of 1917–19 that had been reinterpreted by Gerlach (1980). The other compositional end member—"Type II" gas—was said to have characterized rift-zone eruptions. In this eruptive scenario, magma rises from the mantle and preeruptively degasses at 1- to 6-km-depth from the summit magma reservoir, releasing



**Table 1.** Gerlach's thermodynamic restoration of Jaggar and Shepherd's best 1917–19 gas samples from Halema'uma'u lava lake testify to the care taken in the sampling by Jaggar, and the analysis of the gases by Shepherd's lab.

[Quality rating by Jaggar: E=excellent, G=good. Samples identified with an "R" designation denote Gerlach's restoration (Gerlach, 1980). Both Gerlach's restorations and the original reported analyses are expressed in mole percent. Gerlach's restoration procedure provided the equilibrium temperature,  $f_{O_2}$ , and  $H_2S$  concentration for each sample]

Sample	Date	Quality	CO	CO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	SO <sub>2</sub>	S <sub>2</sub>	H <sub>2</sub> S	HCl	T (°C)	Log $f_{O_2}$	C/S	Atomic H/C
J-8	3/25/1918	E	1.5	48.91	0.49	37.11	11.87	0.04	ND	0.08			4.12	
J-8R	3/25/1918	E	1.51	48.9	0.49	37.09	11.84	0.02	0.04	0.08	1,170	−8.38	4.13	1.49
J-11	3/13/1919	E	0.62	21.89	0.33	64.38	12.52	0.26	ND	0			1.75	
J-11R	3/13/1919	E	1.03	36.69	0.55	40.14	21.06	0.25	0.2	0	1,100	−9.33	1.74	2.17
J-13	3/15/1919	E	0.6	17.54	0.99	69.84	10.73	0.09	ND	0.21			1.63	
J-13R	3/15/1919	E	0.62	17.82	1.01	69.29	10.93	0.03	0.08	0.21	1,175	−8.40	1.63	7.64
J-14	3/16/1919	E	0.48	15.26	0.18	79.16	4.82	0.1	ND	0			3.17	
J-14R	3/16/1919	E	1.52	47.41	0.54	35.09	15.06	0.17	0.15	0	1,100	−9.30	3.15	1.46
J-16	3/17/1919	E	0.58	18.61	0.69	68.38	11.42	0.15	ND	0.17			1.63	
J-16R	3/17/1919	E	0.74	23.21	0.87	60.42	14.31	0.07	0.14	0.21	1,140	−8.84	1.62	5.14
J-17	3/17/1919	G	0.37	11.76	0.59	80.36	6.57	0.24	ND	0.1			1.79	
J-17R	3/17/1919	G	0.62	20.27	1.02	65.95	11.44	0.16	0.32	0.17	1,085	−9.65	1.77	6.45

**Table 2.** Gerlach and Graeber's (1985) volatile budget factored the sequential degassing pathway of parental melt through summit reservoir equilibration and rift zone storage and eruption by considering gas release behavior during a 27-year period of activity (July 1956 to April 1983).

Volatile class	H <sub>2</sub> O			CO <sub>2</sub>			S			Cl			F		
Parental volatiles	18(2) <sup>1,2</sup>	18(2) <sup>3</sup>	100 <sup>4</sup>	38(5) <sup>1</sup>	39(5) <sup>3</sup>	100 <sup>4</sup>	7.6(7) <sup>1</sup>	7.7(7) <sup>3</sup>	100 <sup>4</sup>	0.51(5) <sup>1</sup>	0.52(5) <sup>3</sup>	100 <sup>4</sup>	2.1(2) <sup>1</sup>	2.1(2) <sup>3</sup>	100 <sup>4</sup>
Chamber gas	2(3)	2(3)	10	36(5)	37(5)	95	3.5(9)	3.6(9)	46	0.00(7)	0.00(7)	~0	0.0(3)	0.0(3)	~0
Stored volatiles <sup>5</sup>	16(2)	16(2)	90	2.0(2)	2.0(3)	5	4.1(5)	4.2(5)	54	0.51(5)	0.52(5)	100	2.1(2)	2.1(2)	100
Volcanic gas	3.5(7)	3.6(7)	20	0.4(1)	0.4(1)	1	1.1(2)	1.1(2)	15	0.02(2)	0.02(2)	3	0.01(9)	0.01(9)	~0.4
Residual	2.0(3)	2.1(3)	12	0.31(5)	0.31(5)	1	0.31(3)	0.31(3)	4	0.16(2)	0.17(2)	32	0.72(8)	0.73(8)	34.6
Non-erupted	10(1)	10(1)	58	1.3(2)	1.3(2)	3	2.7(3)	2.7(3)	35	0.33(3)	0.34(3)	65	1.3(1)	1.4(1)	65

<sup>1</sup>Total g × 10<sup>−12</sup> calculated for the period July 1956 to April 1983 and rounded to significant figures.

<sup>2</sup>Parentheses enclose propagated error in preceding digit.

<sup>3</sup>(g per day) × 10<sup>−8</sup> calculated from total g × 10<sup>−12</sup> per the 9,800-day period and rounded to significant figures.

<sup>4</sup>Each category (before rounding) as percent of parental volatile supply.

<sup>5</sup>Assumes equilibration of CO<sub>2</sub> in reservoir melt at 2-km depth.

**Table 3.** Gas composition of parental, stored, and residual volatiles based on the volatile budget of Gerlach and Graeber (1985; table 2).

Volatile class	H <sub>2</sub> O	CO <sub>2</sub>	S	Cl	F
Parental <sup>1</sup>	0.30(2) <sup>4</sup>	0.65(6)	0.130(4)	0.0087(3) <sup>2</sup>	0.0354(20) <sup>5</sup>
Stored <sup>2</sup>	0.27(2)	0.034(3)	0.070(5)	0.0087(3) <sup>2</sup>	0.0354(20)
Residual <sup>3</sup>	0.10(1)	0.015(2)	0.015(1)	0.0080(3) <sup>2</sup>	0.0350(20)

<sup>1</sup>Weight percent concentrations for parental melt oversaturated in CO<sub>2</sub> and chamber conditions. All concentrations calculated except for S, which is based on glass inclusion data.

<sup>2</sup>Weight percent concentrations for reservoir-equilibrated melt at 2-km depth. All concentrations calculated except for S, which is based on data for glassy East Rift Zone submarine basalts.

<sup>3</sup>Mean values for CO<sub>2</sub>, S, Cl, and F in weak fountain spatter. H<sub>2</sub>O value for fountain spatter from the 1983 middle East Rift Zone eruption.

<sup>4</sup>Parentheses enclose propagated error in preceding digit.

<sup>5</sup>Based on stored volatile concentrations.

most of its  $\text{CO}_2$ , along with a small portion of its  $\text{SO}_2$ , as “chamber gas”; the remaining  $\text{SO}_2$ - and  $\text{H}_2\text{O}$ -rich, Type II gas is released through the process of eruption when magma reaches the surface in the rift zone (fig. 8B).

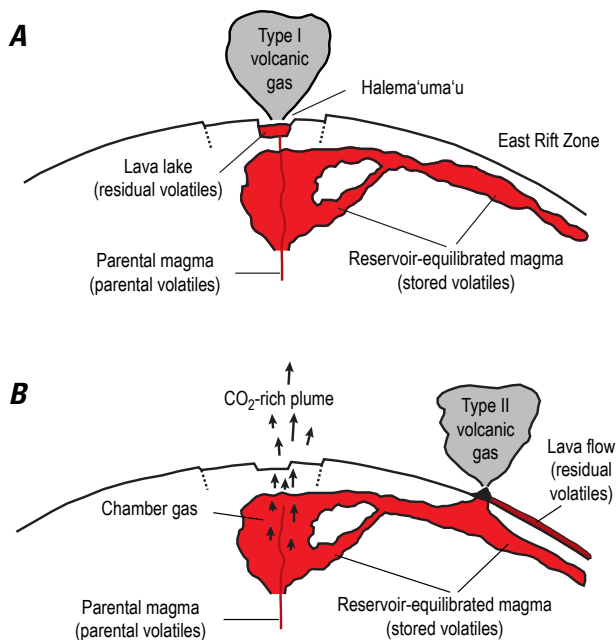
Gerlach rigorously examined the progressive exsolution of volatiles in relation to pressure and depth, using analyses of the Type II gases that were prevalent during the beginning of the Pu‘u ‘Ō‘ō-Kupaianaha eruption.  $\text{CO}_2$ , the least soluble gas, exsolved early during magma ascent at depths of tens of kilometers, followed by  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ , and  $\text{HF}$  (Gerlach and Graeber, 1985; Gerlach, 1986). Working with his 1983 East Rift Zone gas collections, Gerlach (1993) concluded that coexisting lavas effectively buffer  $f_{\text{O}_2}$  from molten temperatures down to several hundred degrees below subsolidus temperatures.

By 1983, when the Pu‘u ‘Ō‘ō-Kupaianaha eruption began, the campaign-style  $\text{SO}_2$ -emission-rate-measurement program started by Casadevall in 1979 had become an integral component of eruption monitoring at HVO. Although Casadevall and Furukawa left HVO to join the newly formed Cascades Volcano Observatory (CVO) in Vancouver, Wash., in 1981, Casadevall remained an active adjunct of HVO for years to come. The regular COSPEC measurements that he initiated and that Barry Stokes took over in 1982 captured a rapid doubling of Kīlauea summit  $\text{SO}_2$  emissions after the start of the East Rift Zone eruption, and airborne  $\text{SO}_2$  and  $\text{CO}_2$  emission-rate measurements at the summit and East Rift Zone affirmed

the previous observations by Paul Greenland and Terry Gerlach (Greenland and others, 1985; Gerlach and Graeber, 1985)—that during rift zone eruptions, Kīlauea magma loses most of its  $\text{CO}_2$  through passive degassing at the summit, while most of the  $\text{SO}_2$  is released in the rift zone eruptive plume (Casadevall and others, 1987).

The March 25 to April 14, 1984, Mauna Loa eruption provided an opportunity to make the first airborne  $\text{SO}_2$  and  $\text{CO}_2$  measurements at that volcano (Casadevall and others, 1984). The initial  $\text{SO}_2$  emission rate, ~70 metric kilotons per day (kt/d), exceeded the dynamic range of the COSPEC during the first week of the eruption. These rates were measured by the Total Ozone Mapping Spectrometer (TOMS) carried aboard the NIMBUS 7 spacecraft until they dropped below its 10-kt/d practical detection limit. After this interval, the COSPEC, reconfigured to measure higher  $\text{SO}_2$ -emission rates, recorded the decline in emissions until the eruption ended.

Greenland continued to explore the volatile-release processes associated with Hawaiian eruptions by combining the gas-chemistry analyses with COSPEC-derived  $\text{SO}_2$  emission rates and geophysical data. He reported the first selenium and tellurium abundances in eruptive gases (Greenland and Aruscavage, 1986) and noted the similarity in  $\text{CO}_2$  depletion between Kīlauea and Mauna Loa summit and rift volatile release during the 1984 Mauna Loa eruption (Greenland, 1987b). At Kīlauea, he used tilt and emission-rate data to estimate the dimensions and rise rate of magma in the eruptive conduit at Pu‘u ‘Ō‘ō, along with pressure/density profiles for the eruptive column (Greenland and others, 1988). Greenland also reconciled and summarized 75 years of eruptive gas study as part of HVO’s Diamond Jubilee (Greenland, 1987a). In his conclusions, he noted that Hawaiian eruptive gases exist fundamentally as either a preeruptively degassed,  $\text{CO}_2$ -depleted form with a molecular C/S ratio of ~0.2, or, in the case of magma arriving directly from the mantle, a  $\text{CO}_2$ -rich form with a molecular C/S ratio of ~2.0. He also showed that the disequilibrium compositions of eruptive-gas samples could be accounted for by assimilation of crustal or meteoric water. Finally, he concluded that the total volatile content of magma stored in the summit reservoir is uniform and less than 0.5 weight percent. Paul Greenland retired in 1986, and although his position was not immediately filled, Barry Stokes kept up the high-quality, long-running  $\text{SO}_2$  emission-rate and summit-fumarole chemistry databases until he left the USGS in 1991.



**Figure 8.** Gerlach and Graeber’s (1985) volatile budget diagram (adapted) showing two end-member eruptive gas types. A, Single-stage degassing of parental magma, with a plume rich in  $\text{CO}_2$  and including  $\text{SO}_2$  and  $\text{H}_2\text{O}$  (Type I volcanic gas), attends sustained summit eruptions. B, Prolonged rift-zone eruptions are associated with two-stage gas release, involving preeruptive venting of  $\text{CO}_2$ -rich chamber gas at summit and  $\text{SO}_2$ - and  $\text{H}_2\text{O}$ -rich gas release (Type II volcanic gas) from rift-zone eruption site.

## Tuning Technologies and Enhancing the Time-Series Database

In 1993, Jeff Sutton joined HVO as staff geochemist. Sutton had worked intermittently at HVO in his role as a chemical-sensors specialist on Moto Sato’s project, studying the geochemistry of gas-forming elements in the 1980s, and he had helped build CVO’s gas-analysis and continuous gas-monitoring capability while a staff member there. In

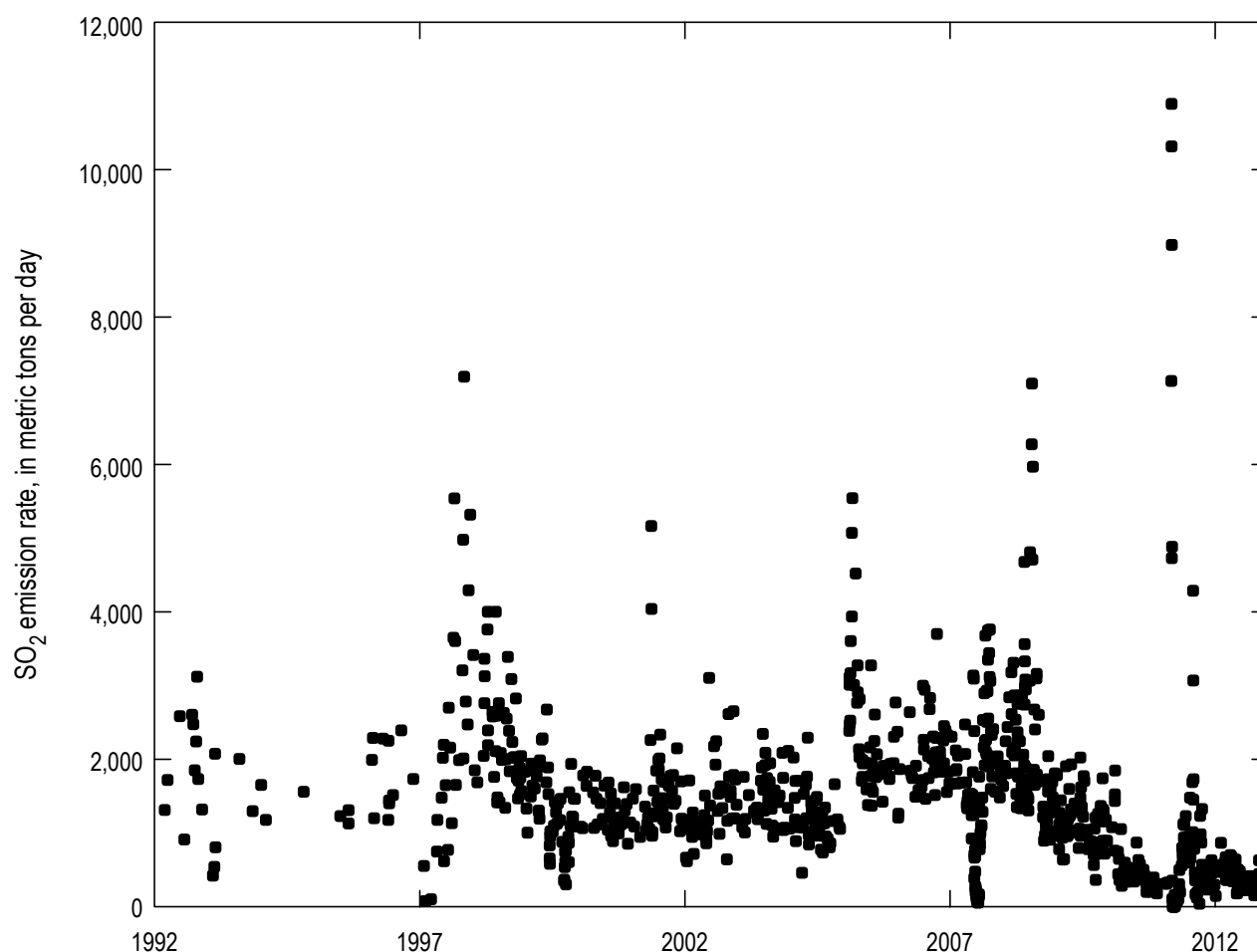
conjunction with his appointment, Tamar Elias became a member of the volcanic-gas-studies group almost a year earlier, after overlapping with Stokes. Elias, a chemist, had been working at HVO in various capacities for several years, as well as with the National Park Service and other agencies, to monitor air quality.

In addition to the continuation of the Pu‘u ‘Ō‘ō–Kupaianaha eruption, the early 1990s were a time of geothermal energy development on Kīlauea’s lower East Rift Zone. In support of an environmental impact assessment related to this development, Sutton and Elias reported the effects of volcanic emissions on ambient-air characteristics through a literature review. A series of campaign-style field measurements of ambient air and rainwater at 15 sites at Kīlauea’s summit and along the East Rift Zone to the coastal lava entry documented the mostly localized environmental effects (Sutton and Elias, 1993a).

Because most of the SO<sub>2</sub> being emitted from Kīlauea was coming from Pu‘u ‘Ō‘ō and other scattered East Rift Zone sources, Elias began making routine vehicle-based

SO<sub>2</sub>-emission-rate measurements along Chain of Craters Road in 1992 (fig. 9). Before these measurements commenced, HVO had relied on sporadic, tripod-based COSPEC SO<sub>2</sub> data collections near Pu‘u ‘Ō‘ō to measure rift zone emissions (Elias and others, 1998). Fixed-wing airborne measurements, though satisfactory for episodes of high lava fountaining, were expensive, time consuming, and less acceptable for measuring the low-level, ground-hugging plumes that characterized the eruption, beginning with the continuous effusive Kupaianaha phase in 1986. Also, a comparison between contemporaneous tripod- and vehicle-based East Rift Zone COSPEC measurements indicated that plume-source geometry and light-propagation issues contributed to tripod data that were consistently lower than vehicle-based emission-rate measurements, and that the vehicle-based measures were probably more accurate (Andres and others, 1989; Elias and others, 1998).

The closing years of the 1990s brought an additional technological advance in HVO gas studies—the field-portable LI-COR Biosciences CO<sub>2</sub> analyzer. This direct-sampling



**Figure 9.** Vehicle-based SO<sub>2</sub> emission-rate measurements were shown to be an effective and economical means of tracking activity at Pu‘u ‘Ō‘ō and other East Rift Zone eruption sites. These emissions dwarfed those of the summit by nearly 10:1 until several months after start of 2008 summit eruption, when preeruptive degassing at summit caused the SO<sub>2</sub> emission rate from Pu‘u ‘Ō‘ō to decrease. In this plot, each data point represents an average of several transects through plume. Error bars are omitted for clarity, but uncertainty is generally within 30 percent of the measured value.



instrument applied the same nondispersive-infrared-spectroscopic approach to measuring  $\text{CO}_2$  that had been used with the Miran analyzer during the early days of the Mount St. Helens eruptions (Harris and others, 1981); however, improved sensitivity and updated digital signal processing made the LI-COR analyzer superior both for vehicle-based and airborne gas studies (Gerlach and others, 1997). Gerlach and coworkers used the LI-COR analyzer at Pu‘u ‘Ō‘ō in an airborne (fixed wing) mode to simultaneously measure both  $\text{SO}_2$  emission rate, by COSPEC, and  $\text{SO}_2$  concentration, by Fourier transform infrared (FTIR) spectroscopy (Gerlach and others, 1998; McGee and Gerlach, 1998). The method they developed to measure the  $\text{CO}_2$  emission rate at Pu‘u ‘Ō‘ō used the molecular C/S ratio in the core of the gas plume. The product of the  $\text{SO}_2$  emission rate, the molecular C/S ratio, and the molecular-weight ratio yielded the  $\text{CO}_2$  emission rate.

The  $\text{CO}_2$  emission rate measured in the Pu‘u ‘Ō‘ō plume, 0.300 kt/d, supported earlier assertions by both Gerlach and Graeber (1985) and Greenland (1984) that the magma being erupted at Pu‘u ‘Ō‘ō had already been degassed of most of its  $\text{CO}_2$ . The airborne plume molecular C/S ratio reported was similar to that measured in eruptive-gas samples from Pu‘u ‘Ō‘ō fumaroles during the first 12 years of the eruption, providing support for the new methodology (Gerlach and others, 1998).

## Eruptive Changes Lead to a Better Appreciation of Volcanic Gas Emissions as a Volcanic Hazard

The spectacular high lava fountains that occurred from 1983 to mid-1986 released  $\text{SO}_2$  from Pu‘u ‘Ō‘ō at rates ranging from 5 to 32 kt/d (Casadevall and others, 1987). Typically, however, these episodes were brief, lasting 24 hours or less (Heliker and Mattox, 2003). During the nearly month-long intereruptive pauses,  $\text{SO}_2$  emissions commonly totaled less than 0.5 kt/d for the summit and East Rift Zone combined (Casadevall and others, 1987; Chartier and others, 1988). For the first several years of East Rift Zone activity, these multiweek pauses resulted in greatly reduced  $\text{SO}_2$  release, giving ample time for high-fountaining gas emissions to dissipate (Sutton and Elias, 1993b).

The continuous lava effusion and consequent gas release that produced the Kupaianaha lava shield ~3 km downrift of Pu‘u ‘Ō‘ō, beginning in 1986, resulted in an accumulation of volcanic gases downwind of Kīlauea’s summit and East Rift Zone sources, especially on the leeward (west) coast of the island (fig. 10). By 1987, island residents from the Ka‘ū and Kona Districts, especially, began reporting negative health symptoms that included breathing difficulties, headaches, eye irritation, and general flulike symptoms. The term “vog,” an Island of Hawai‘i-coined portmanteau for “volcanic smog,” caught on and eventually became used worldwide by communities impacted by nearby volcanoes. As the resident source of data and hazards information related to eruptive emissions, HVO was consulted about volcanic air pollution

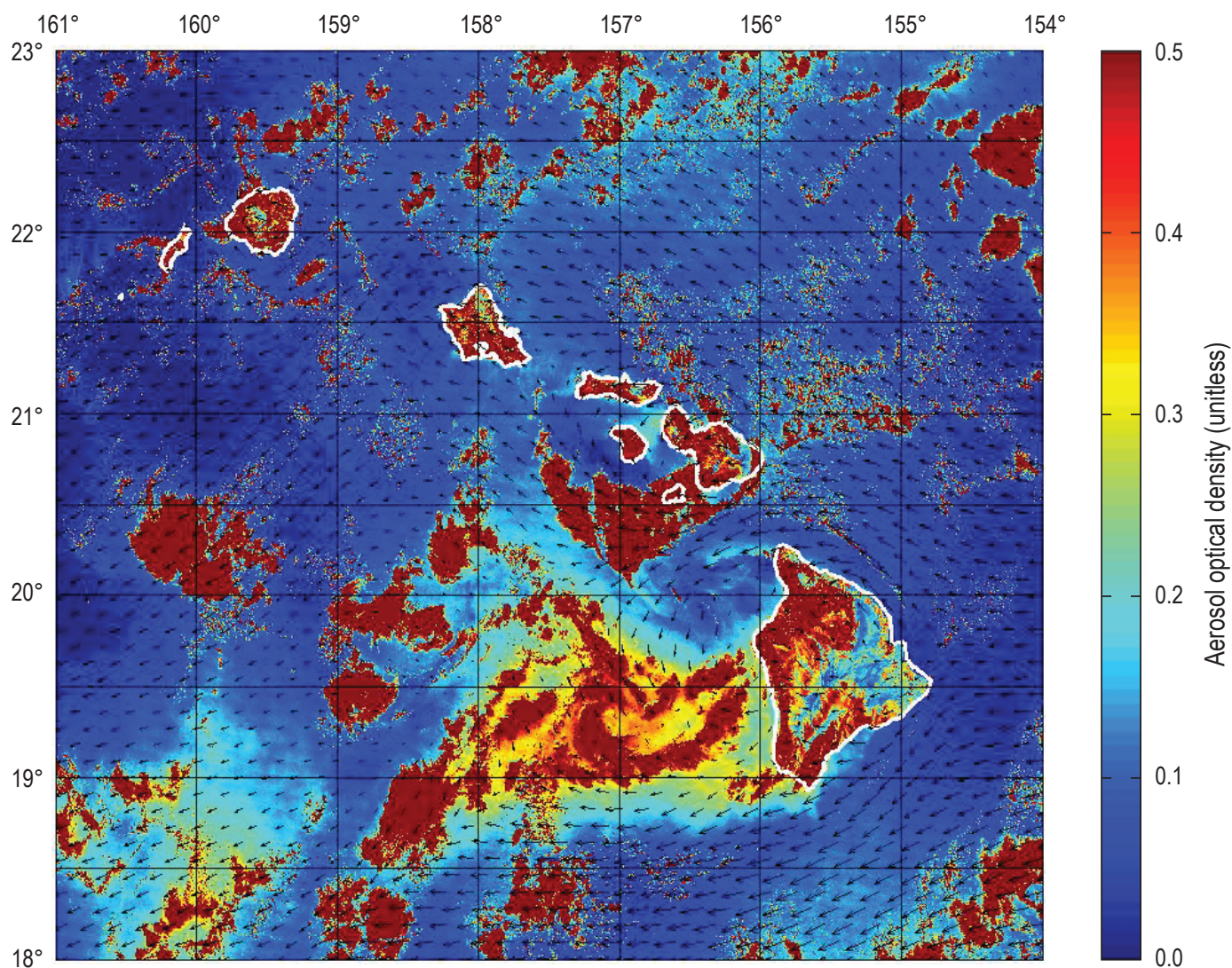
extensively by County, State, and Federal agencies, as well as health studies researchers. The conversion of  $\text{SO}_2$  to acidic sulfate aerosol during transport and the subsequent rainout of these acidic eruptive products into water-catchment tanks, especially on the island’s east coast, caused leaching of substantial amounts of lead and copper into domestic drinking-water supplies. Clinical tests confirmed high levels of lead in the blood of some downwind residents (Sutton and others, 1997). The discovery of this secondary volcanic hazard resulted in a countywide ban on the availability of lead-containing roofing materials and plumbing supplies (Sutton and Elias, 1993b).

As the eruption continued, HVO became an active voice in a Vog Task Force convened by Hawai‘i County to understand and manage the growing impact of volcanic gas emissions on island life. HVO also participated in vog symposia held on the Island of Hawai‘i and on O‘ahu (Casadevall and others, 1991; Chuan, 1991; Gerlach and others, 1991; Sutton and Elias, 1996, 1997). HVO gas geochemists began making frequent presentations to schools and community groups and served as a source of review for health studies professionals seeking to understand the nature of volcanic-emission sources and the physical aspects of Kīlauea’s plume dispersion. With its knowledge of and perspective on emission-source parameters, along with the physical science governing vog distribution, HVO staff produced a USGS Fact Sheet that helped answer continuing requests for information about the topic (Sutton and others, 1997).

## The 2000s: Examining Gas and Geophysical Data Together on a Common Time Base

### $\text{CO}_2$ and $\text{SO}_2$ Emissions Reflect Magma-Supply and Eruption Rates

The technological explosion of the 1960s through 1990s, and the eruptive activity at Kīlauea and Mauna Loa, produced a developmental watershed, both of volcanic gas study methods and of reasoned conceptual models for active volcanic processes in Hawai‘i and elsewhere. The growing database of  $\text{SO}_2$  emission rates at HVO provided insights into Kīlauea’s plumbing system, especially the relation between gas emissions, seismicity, and lava effusion rates. The rapid jump in summit  $\text{SO}_2$  emission rates in 1983 at the beginning of the East Rift Zone eruption and the decline in summit  $\text{SO}_2$  release in 1991 during shutdown of the Kupaianaha vent affirmed the close magmatic connection between Kīlauea’s summit and East Rift Zone. Summit  $\text{SO}_2$  emission rates were also observed to correlate with shallow, short-period seismicity beneath the caldera but not with long-period



**Figure 10.** Image of the Hawaiian Islands from the Moderate Resolution Imaging Spectroradiometer (MODIS) carried aboard the National Aeronautics and Space Administration's Aqua and Terra polar-orbiting satellites, showing Kīlauea's volcanic-aerosol plume, which results from primary particles emitted directly from Kīlauea's vents, and secondary particles formed by chemical conversion of  $\text{SO}_2$  to acidic sulfate aerosol. Under prevailing northeasterly trade-wind conditions, these emissions are carried from Kīlauea's eruptive vents southward, where wind patterns wrap around southern tip of island and send emissions northward along leeward coast. Warmer colors (yellow and orange) depict increasing aerosol loading as  $\text{SO}_2$  is gradually converted to submicron-size droplets of sulfuric acid and particles of acidic and neutralized sulfates.

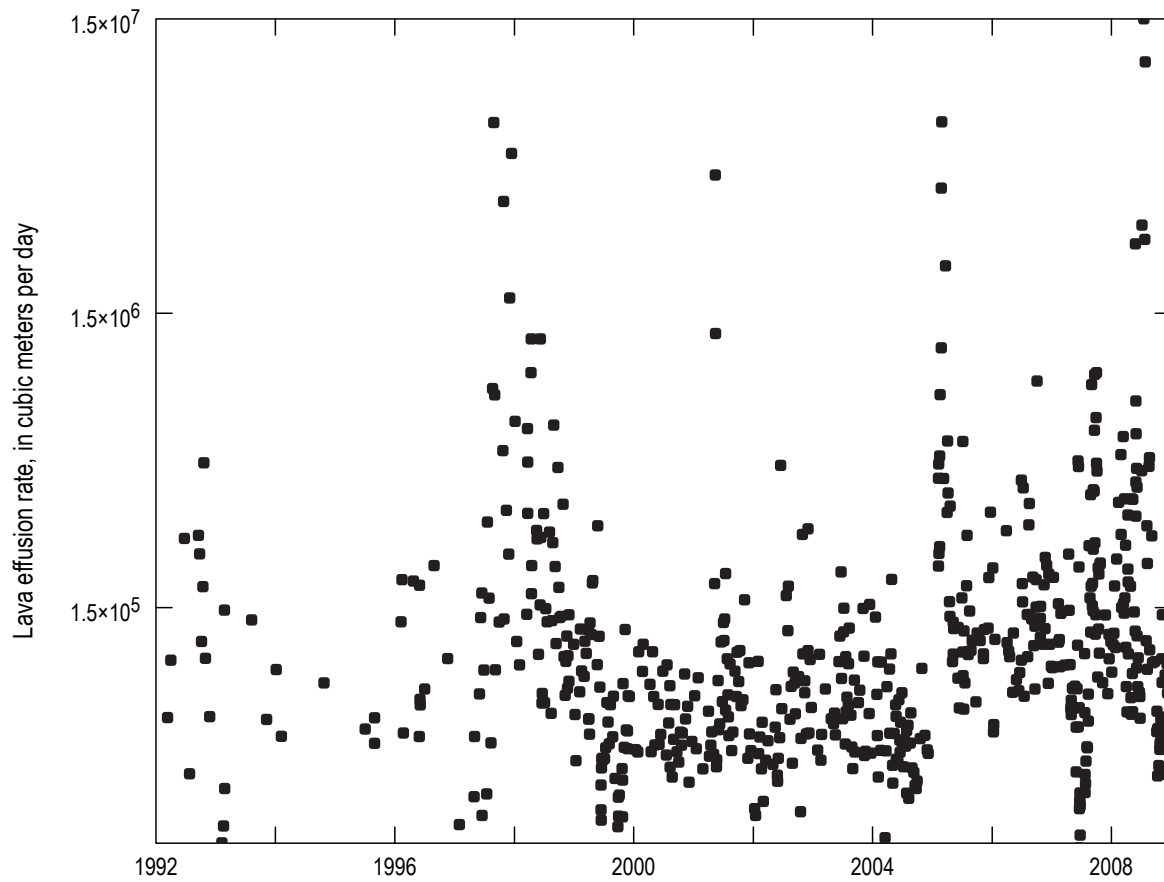
seismic events, as had been demonstrated at more silicic systems (Sutton and others, 2001).

The relation between East Rift Zone  $\text{SO}_2$  release and lava effusion reported by Sutton and others (2001) was subsequently used to derive a continuous lava-effusion rate record for the first 20 years of the Pu'u 'Ō'ō-Kupaianaha eruption (Sutton and others, 2003). The long-running record of eruptive- $\text{SO}_2$ -derived lava effusion rates were compared with direct geologic observations and with effusion rates determined by very-low-frequency (VLF) electromagnetic profiling of lava transport through master lava tubes. The geochemical and geophysical methods produced total volume estimates for the eruption that agreed with one another within 10 percent. Such a good agreement increased confidence in both of these remote techniques for effusion-rate monitoring and, simultaneously,

provided an additional tool for obtaining this fundamental volcano-monitoring metric. East Rift Zone  $\text{SO}_2$  emission rates were especially important for derivation of lava effusion rates during 2003–08, when changes on the lava flow field resulted in the interruption of routine VLF measurements due to a lack of long-term accessible lava tubes with skylights (fig. 11).

By the late 1990s, it was also becoming possible to measure  $\text{CO}_2$  emission rates on a regular basis, thanks to Gerlach and others (1998, 2002), who adapted the airborne molecular C/S ratio technique of  $\text{CO}_2$  emission-rate measurement that they had developed earlier at Pu'u 'Ō'ō for vehicle-based traverses. At Kīlauea's summit, they reported an average  $\text{CO}_2$  emission rate of  $8.5 \pm 0.3$  kt/d between 1995 and 1999. This value, several times higher than what Greenland and others (1985) reported earlier, possibly resulted because the earlier measurements





**Figure 11.** Kilauea East Rift Zone lava effusion rates over time, integrated and computed from a combination of  $\text{SO}_2$  emission rates and flow mapping, have been shown to agree to within 10 percent of lava effusion rates estimated by flow mapping and very low frequency (VLF) electromagnetic measurements (Sutton and others, 2003). When absence of a master lava tube made VLF measurements impractical during 2003–08, HVO relied upon  $\text{SO}_2$ -derived effusion rates. These gas-based effusion rates captured refilling of Pu'u 'Ō'ō in 1997 for the first time in more than 10 years. Similarly, eruptive surges in 2002 and 2005 were tracked with this remote technique. Error bars are omitted for clarity, but uncertainty is generally within 40 percent of the measured value.

relied on cross-sectional profiling of a ground-hugging plume that was difficult to measure in an airborne mode. Using the estimated magma supply rate of Cayol and others (2000), Gerlach and others (2002) revised upwards the estimated  $\text{CO}_2$  content of the parental magma (see table 2), from 0.65 to 0.7 weight percent, and they suggested that  $\text{CO}_2$  emission-rate measurements could routinely serve as an effective proxy for magma supply monitoring (a proposal that proved important; see section below entitled “A Case Study: The 2003–12 Eruptive Sequence”). Accordingly, HVO adapted the vehicle-based method of Gerlach and others (2002) and made it operationally practical by replacing the cumbersome FTIR spectrometer that had initially been used to measure ambient  $\text{SO}_2$  concentration with a similarly sensitive, but less complex, electrochemical instrument. Using this revised measurement strategy, HVO continued to update the  $\text{CO}_2$  emission-rate database (fig. 12).

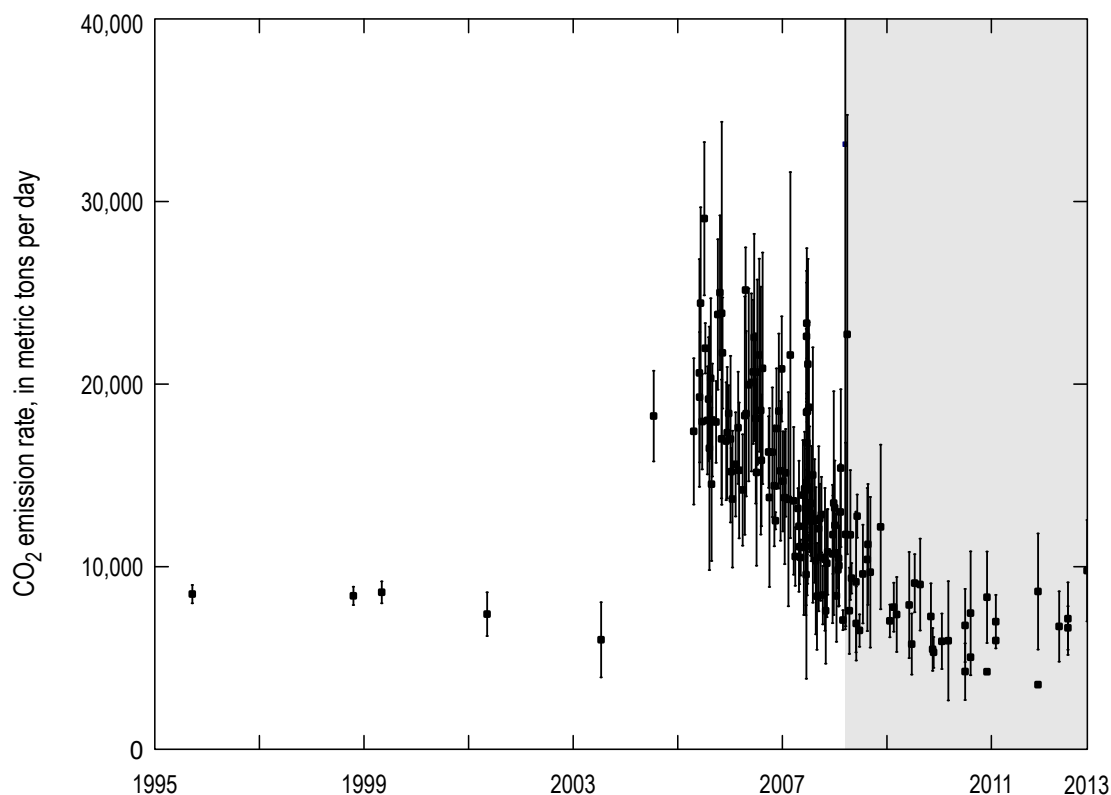
Gas emission-rate studies were evolving on other fronts, as well. Although analog emission-rate data acquisition and reduction had been converted to digital by the early 2000s, the growing availability of low-cost, miniaturized ultraviolet (UV) spectrometers provided an attractive alternative to the expensive and cumbersome COSPEC. In collaboration with

colleagues Keith Horton and Harold Garbeil of the University of Hawai'i, Mānoa, HVO tested and implemented a version of this technology designed and built by Horton and Garbeil and dubbed the FLYSPEC, owing to its small size (Elias and others, 2006; Horton and others, 2006). The FLYSPEC used the correlation spectrometry approach of standardizing field measurements in-situ by calibrating experimental data with known  $\text{SO}_2$  concentration cells measured in the field (fig. 13). Data acquisition and reduction software automatically merged  $\text{SO}_2$  concentration-pathlength data with time-synchronized Global Positioning System (GPS) data, and readily incorporated the LI-COR  $\text{CO}_2$  measurement parameters and the electrochemical  $\text{SO}_2$  and  $\text{H}_2\text{S}$  concentration data needed to calculate  $\text{CO}_2$  and  $\text{H}_2\text{S}$  emission rates.

### Fourier Transform Infrared Spectroscopy Links Short-Term Eruptive Processes to Individual Gas Species

A further advance in gas studies at HVO came in 2004 with the arrival of Mendenhall Postdoctoral Fellow Marie





**Figure 12.** Kilauea summit  $\text{CO}_2$  emission rates over time are related to long-term changes in magma supply to volcano. These rates, steady from 1995 to 2003, increased drastically in 2004, signaling a magma-supply surge that peaked in 2005–06 and then began a steady decline for the next several years as magma supply to the volcano waned. Error bars represent the standard deviation of several transects through plume. Values shown beginning in early 2008 (shaded region) are underestimates due to complications in gas emission rate measurements associated with summit eruptive activity (Elias and Sutton, 2012).

Edmonds, who characterized the summit and rift zone emissions of  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and other gases using open-path Fourier transform infrared (OP-FTIR) spectroscopy. In this field measurement technique, infrared (IR) energy from a hot lava source, an IR lamp, or the sun is measured as it passes through, and is absorbed by, the volcanic plume along an open atmospheric path. Individual gas species, including  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{HCl}$ ,  $\text{HF}$ , and  $\text{COS}$ , absorb light energy and can be quantified within different wavelength regions of the spectrum. An example of the utility of the OP-FTIR approach at Kilauea is provided by Edmonds and Gerlach (2006), who studied the composition of the coastal-entry plume and determined that intense  $\text{HCl}$  generation could occur at moderate-size lava ocean entries, creating a significant local hazard.

Edmonds and Gerlach (2007) also examined short-term variations in gas emissions at eruptive vents within Pu‘u ‘Ō‘ō crater using OP-FTIR spectroscopy in 2004 and 2005. In their study, they characterized three distinct types of gas release: (1) persistent, continuous release of  $\text{H}_2\text{O}$ -rich,  $\text{CO}_2$ -poor gas that occurred when magma ascended with bubbles that burst at the surface; (2) “gas-piston” release, characterized by loud jetting and increased glow within small eruptive vents (but probably different from the more traditional gas piston events at Kilauea later described by Patrick and others, 2011a) and



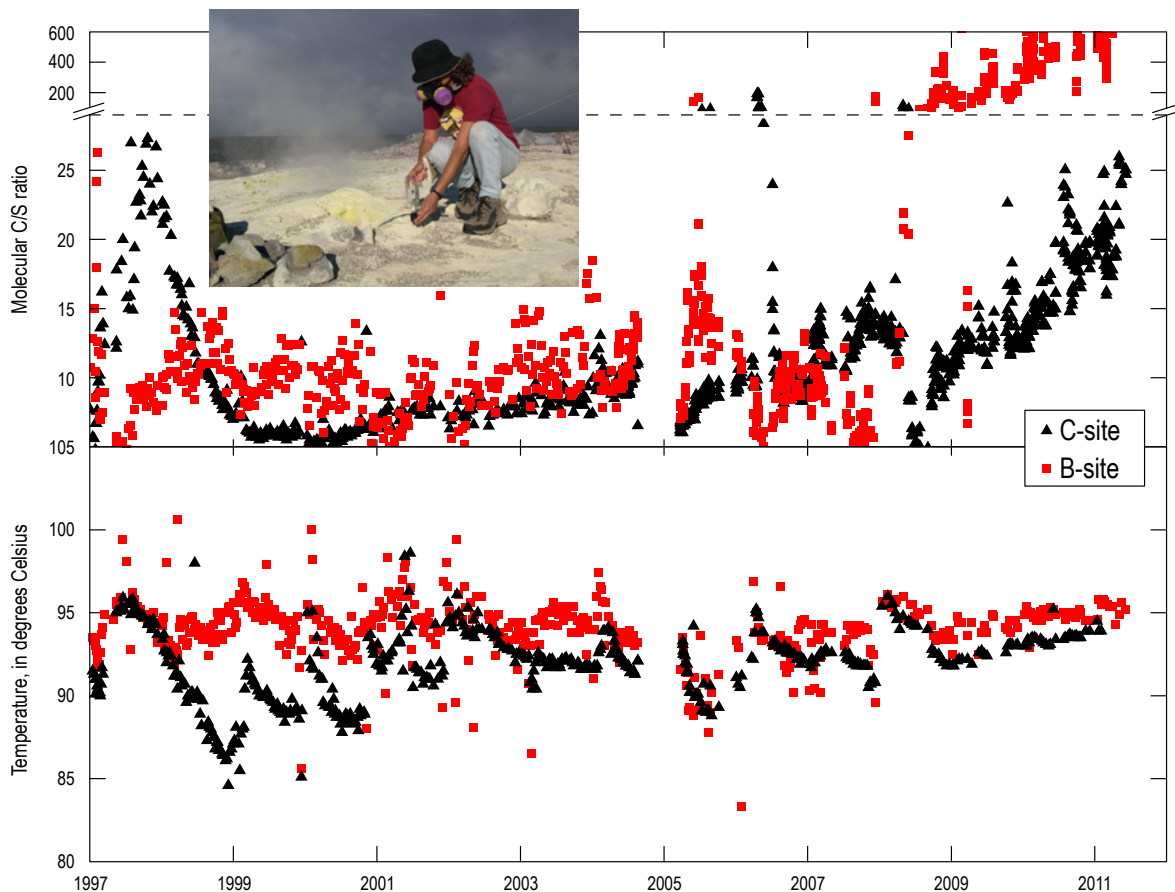
**Figure 13.** Miniaturization of ultraviolet spectrometers resulted in improved  $\text{SO}_2$  emission-rate measurements. With colleagues Horton and Garbeil of the University of Hawai‘i, HVO codeveloped the FLYSPEC (left). For six months, beginning in late 2003, FLYSPEC measurements were made in parallel with the COSPEC (right) before COSPEC use was discontinued.

accompanied by the release of  $\text{CO}_2$ -rich gas, interpreted to be driven by gas slugs rising from depths of several hundred meters; and (3) gas release associated with lava spattering, due to quiescent coalescence of large,  $\text{H}_2\text{O}$ -rich and  $\text{SO}_2$ - and  $\text{CO}_2$ -poor bubbles. In a follow-up study, Edmonds and others (2009) used the 2004–05 Pu‘u ‘Ō‘ō data to develop an exsolution model for halogen gas release, recognizing that this process occurs principally at very shallow depths (tens of meters or less) in the magma column. Using synchronous  $\text{SO}_2$  concentration and emission rates, they reported HCl and HF emissions from Pu‘u ‘Ō‘ō of 25 and 12 t/d, respectively.

Regular OP-FTIR-spectroscopic measurements quickly became an important part of the eruption-monitoring strategy at HVO. As a remote technique, OP-FTIR spectroscopy allowed HVO staff to make more detailed measurements of gas chemistry with more flexibility and safety than ever before. Although routine gas-bottle collections with subsequent laboratory GC analysis were still conducted at long-lived summit fumaroles (fig. 14), regular collection of uncontaminated samples at active eruptive vents was difficult. In combination with  $\text{SO}_2$  emission-rate measurements, OP-FTIR-derived gas concentrations could

be compared in ratio fashion with  $\text{SO}_2$  concentrations in the volatile matrix and used to estimate emission rates of principal gases ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , HCl, HF, CO, COS) emitted at vents that were impractical to sample with gas bottles—for example, in lava lakes at both Kīlauea’s summit and Pu‘u ‘Ō‘ō.

The growing database of different types of volcanic gas measurements meant that HVO could study eruptive activity with unprecedented depth. Regular  $\text{CO}_2$  emission rates, tied to magma supply, and East Rift Zone  $\text{SO}_2$  emission rates, indicating lava effusion rate, were linked analytically via OP-FTIR spectroscopy with other principal volcanic gases, providing a view encompassing a wide range of gas solubilities and associated subsurface conditions. Such applications also facilitated comparison of gas data with other geologic and geophysical monitoring parameters. For example, the World Wide Web-based Volcano Analysis and Visualization Environment (VALVE) permitted rapid, simultaneous display, on a common time base, of many types of data collected by HVO (Cervelli and others, 2002). With the new tool, plotting of time-series gas emissions or continuous monitoring of concentration data, for example, against seismicity or surface



**Figure 14.** Easy access to Kīlauea’s summit fumaroles and their close proximity to HVO’s analytical laboratory have enabled fumarole sampling as a part of routine gas monitoring. Inset, HVO geochemist Tamar Elias samples gases from a boiling-point solfatara using an evacuated bottle (the same technique has been in use for over for more than 30 years). Molecular C/S ratio (upper plot) and temperature (lower plot) over time for fumarole sampling sites on southwest (B-site) and north (C-site) rim of Halema’uma’u Crater. Emissions from these sites are sensitive to major changes in conditions in summit magmatic system, as well as to sulfur-gas scrubbing caused by seasonal rainfall events.

deformation became possible. This new capability helped set the stage for interactive and ongoing interpretation of volatile emissions in the broader context of Kīlauea's ongoing eruptive activity.

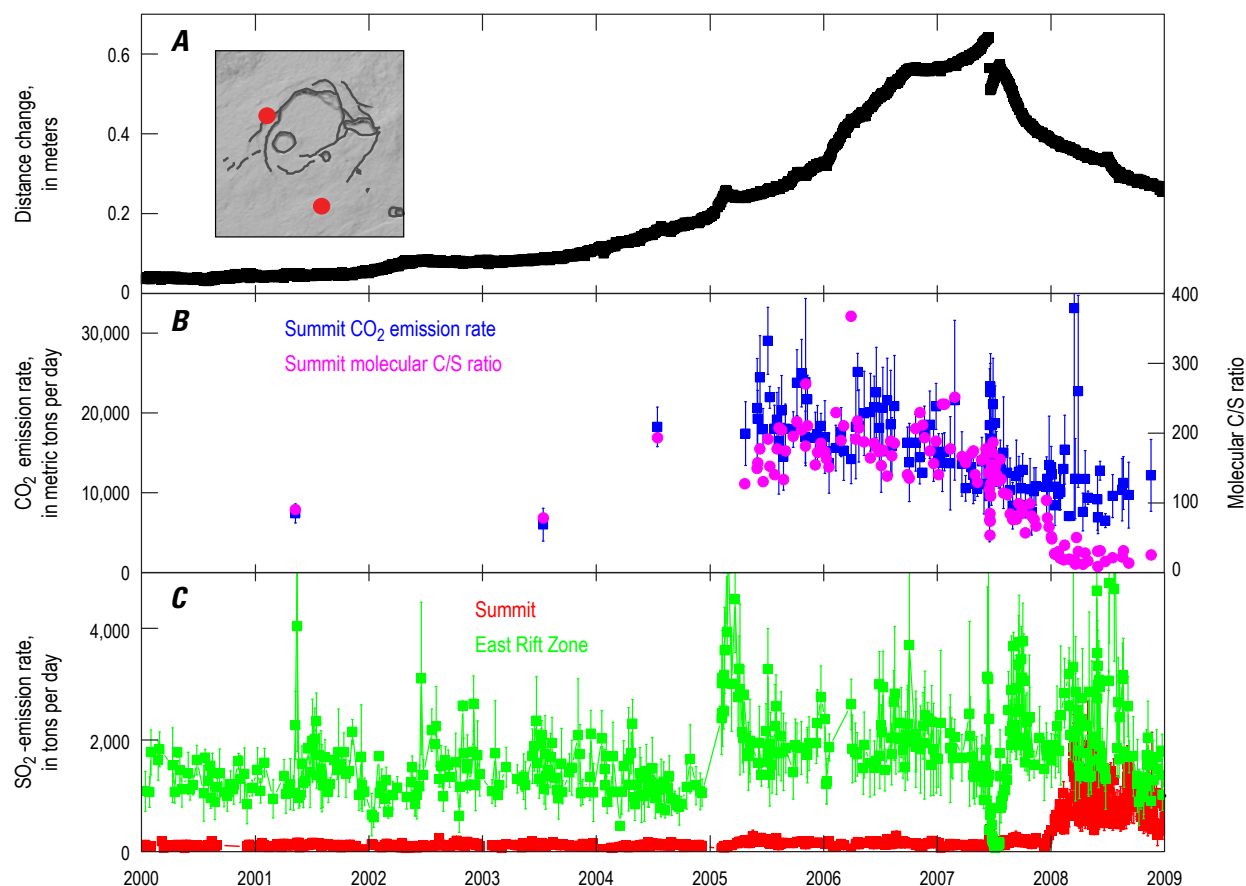
## A Case Study: The 2003–12 Eruptive Sequence

From 2000 through mid-2003, CO<sub>2</sub> emission rates at Kīlauea's summit approximately followed the long-term average of 8.5 kt/d, indicating an overall steady magma supply rate to the volcano. During the same interval, the absence of significant change along a caldera-crossing GPS baseline indicated little summit deformation and an eruption rate that was keeping up with, or slightly outpacing, magma supply (Cervelli and Miklius, 2003; Poland and others, 2012). Relatively consistent East Rift Zone SO<sub>2</sub> emissions suggested a steady lava effusion rate, consistent with the inference of a constant magma supply.

In late 2003, however, conditions began to change. The summit-crossing GPS baseline began to increase in length, and

uplift began to occur within the summit caldera (fig. 15A). By mid-2004, the summit CO<sub>2</sub> emission rate had increased by ~250 percent (fig. 15B), indicating at least a doubling of the magma supply rate (Poland and others, 2012). At about the same time, an increase in the East Rift Zone SO<sub>2</sub> emission rate (fig. 15C) indicated a near-doubling of the eruption rate as well. Other gas-studies measurements corroborated the increase in magma supply. Continuous CO<sub>2</sub> concentration monitoring within the North Pit instrument vault, located near the north edge of Halema'uma'u Crater, began to show a marked rise in CO<sub>2</sub> concentration at the beginning of 2004. The rise in subsurface CO<sub>2</sub> to hazardous levels in the summit caldera caused Hawai'i Volcanoes National Park to close caldera lava-tube caves to researchers and visitors alike in 2005.

Summit uplift continued into 2006 and began to extend outward into Kīlauea's Southwest Rift Zone. With the supply of magma to the summit outpacing the East Rift Zone's capability to erupt lava at the increased volume rate, the upper East Rift Zone plumbing failed in June 2007. This failure manifested as a dike that intruded the upper East Rift Zone, resulting in a small eruption on June 19. The Father's Day eruption, as it



**Figure 15.** Cross-caldera extension (A, measured between GPS sites that span caldera [red dots in the inset map]) and CO<sub>2</sub> emission rate and ambient molecular C/S ratio (B) captured an increase in magma supply to Kīlauea beginning in 2003 that resulted in an increase in East Rift Zone effusion rate, reflected by an increase in East Rift Zone SO<sub>2</sub> emission rates by 2005 (C). Although CO<sub>2</sub> emission rates began to decline as early as 2006, Kīlauea's summit continued to expand, with supply outpacing effusion until 2007, when an upper East Rift Zone intrusion and eruption in June relieved magmatic pressure somewhat. Magma withdrawal likely lowered summit-reservoir pressure, causing an increase in SO<sub>2</sub> emission rate from the summit magma reservoir and a consequent decrease in molecular C/S as magma worked its way toward the surface in early 2008.



became known, was volumetrically small—approximately  $1,500 \text{ m}^3$  (Poland and others, 2008)—but the emplaced dike exceeded  $15 \times 10^6 \text{ m}^3$  in volume (Montgomery-Brown and others, 2010). Gas measurements at the summit during the activity paradoxically recorded a spike in the  $\text{SO}_2$  emission rate, despite the fact that magma was clearly draining from beneath the summit caldera, as indicated by deflationary deformation. This spike was interpreted as an indicator of decompression of the summit reservoir due to magma withdrawal (Poland and others, 2009).

The summit  $\text{SO}_2$  emission rate after the Father's Day eruption became steady once more, though somewhat elevated, relative to the pre-Father's Day eruption period. The summit  $\text{CO}_2$  emission rate, however, continued the linear decline that had begun in 2006, and the corresponding molecular C/S ratio in the summit gas plume dropped incrementally for the first time in more than 3 years (fig. 15B). As 2007 came to a close, summit caldera seismicity began to increase, and, after a large rainfall event in early December that effectively scrubbed summit  $\text{SO}_2$ , those emissions began to climb, as well.

At the beginning of 2008, several gas-release effects were observed almost simultaneously. The summit  $\text{SO}_2$  emission rate began to increase more sharply and, by late January, intermittent signal saturation indicated that FLYSPEC retrievals had begun to underestimate actual  $\text{SO}_2$  emission rates (Elias and Sutton, 2012). Even as underestimates, these values were the highest measured in more than 25 years (fig. 6). Meanwhile, the summit  $\text{CO}_2$  emission rate continued its monotonic decline. Analysis of gases from the two long-monitored summit fumaroles indicated that, although the  $\text{CO}_2$  concentrations in these solfatara had remained fairly steady during the previous year, the  $\text{SO}_2$  concentrations had risen significantly. The net effect was that by mid-January 2008, gases being emitted from these fumaroles had taken on a Gerlach and Graeber (1985)  $\text{CO}_2$ -depleted,  $\text{SO}_2$ - and  $\text{H}_2\text{O}$ -rich, Type II eruptive gas composition (fig. 14).

The composite gas signature of rising summit  $\text{SO}_2$  emissions and an eruptive molecular C/S-ratio signature in fumarole gases, along with a declining  $\text{CO}_2$  emission rate, indicated a shallow process at work, possibly even a shallowing of magma. Summit tremor also increased with the rising  $\text{SO}_2$  emission rate but, enigmatically, the overall summit deformation signal was one of deflation (fig. 15A). By mid-February, the summit  $\text{SO}_2$  emission rate was high enough to produce hazardous  $\text{SO}_2$  concentrations adjacent to Halema'uma'u Crater. Hawai'i Volcanoes National Park personnel were responding to an increasing number of respiratory emergencies in the vicinity, and in late February, in consultation with HVO, they closed the area adjacent to, and downwind of, Halema'uma'u.

The appearance of a new, vigorously fuming area beneath the Halema'uma'u visitor overlook was noted on March 12, 2008, which, a week later, was followed by the explosive opening of a new eruptive vent at Kīlauea's summit—the first summit eruption since 1982 (fig. 16; Houghton and others, 2011; Patrick and others, 2011b). With continued widening over time, a lava lake deep within the growing vent became visible from

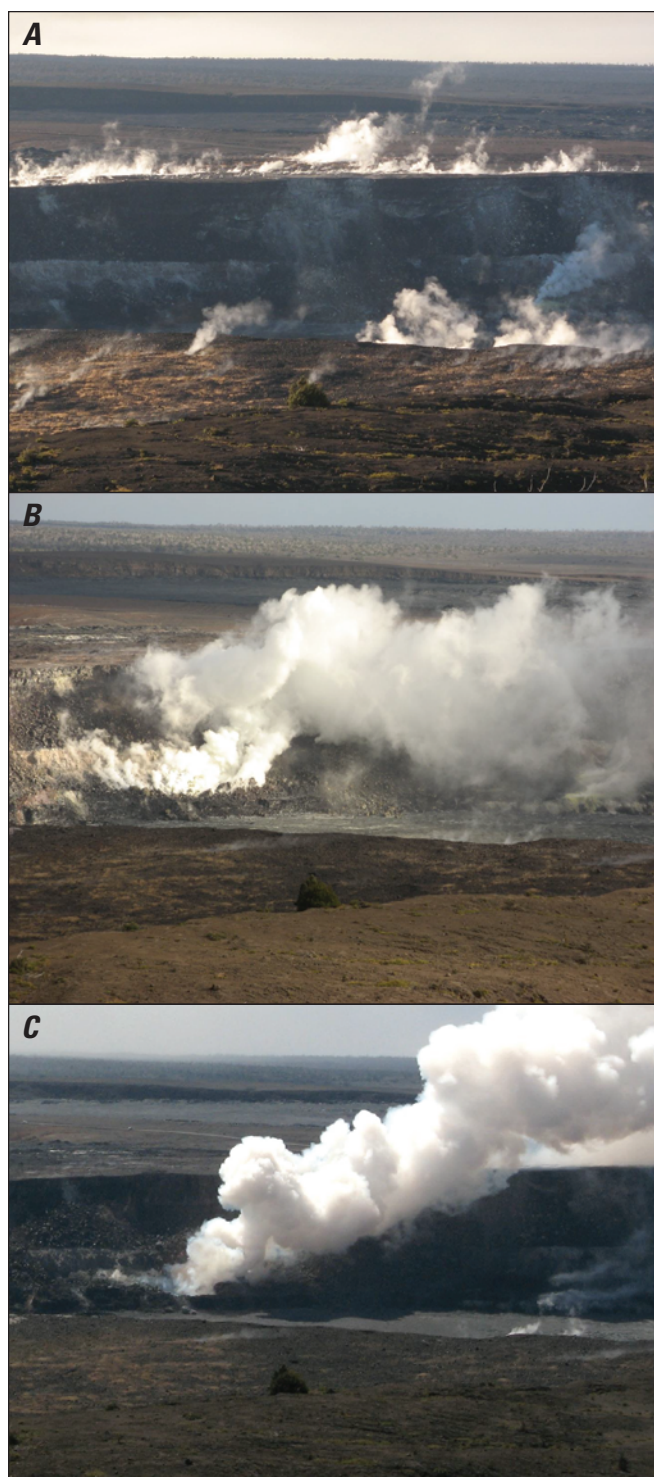
the crater rim, providing an opportunity to study eruptive gas chemistry directly, using OP-FTIR spectroscopy (fig. 17). The composition of emitted gases early in the eruption, similar to that of the East Rift Zone eruptive gases reported by Greenland (1986, 1987b), also fit the description of a Gerlach and Graeber (1985),  $\text{CO}_2$ -depleted,  $\text{SO}_2$ - and  $\text{H}_2\text{O}$ -rich, Type II eruptive gas (Sutton and others, 2009).

## Discussion and Conclusions

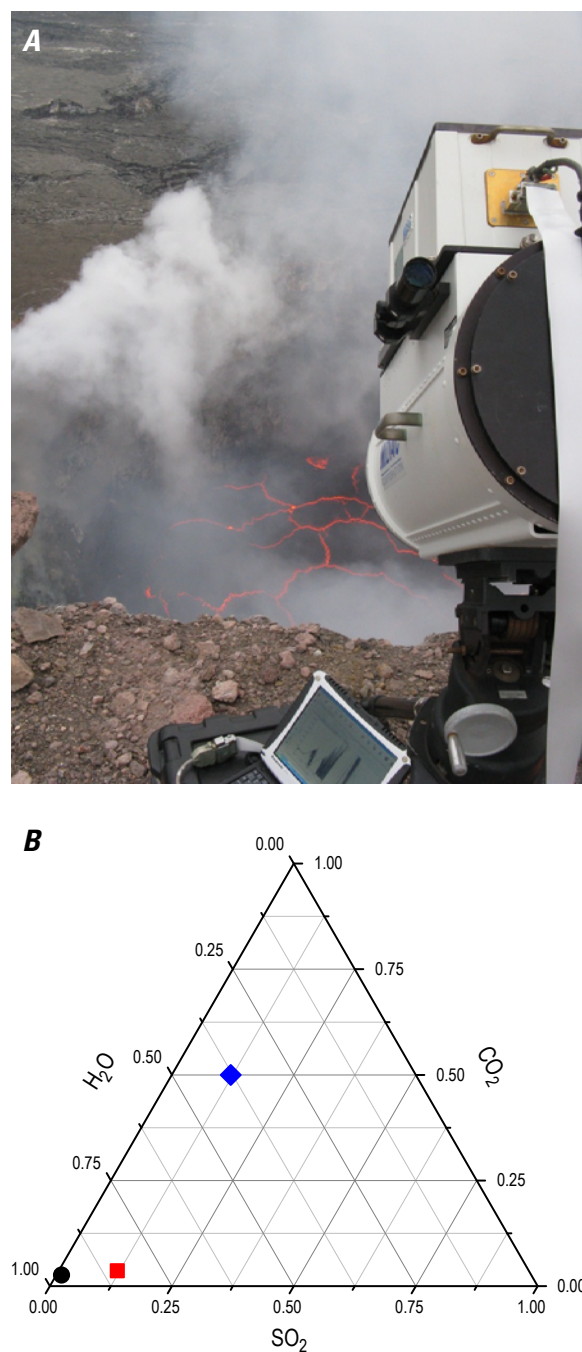
The first hundred years at HVO began with academic-style volcanic gas studies probing the chemical properties of volcanic exhalations. In 1912, the fundamental question about volcanic gas being asked, not only in Hawai'i but at volcanoes worldwide, was "What's in it?" Not surprisingly, this basic question was not so easy to answer a century ago. Sampling strategies were a speculative venture at that time; there was no procedure for sampling gases, because knowledge of volcanic gas content was lacking. Paradoxically, the reason why gas composition was unknown was that hazardous, hot, and corrosive field conditions made gas sampling more challenging than anything ever tried, even in industry. Once the hard-won 1912–24-era samples—as rare and precious as Moon rocks—were collected in fragile glass vials and transported by ship back to the Geophysical Laboratory in Washington, D.C., the laboratory analyses themselves had to be carried out at a higher level of sensitivity than had been attempted previously. First, however, analysts needed to examine the samples qualitatively to determine which chemical species were present before they could attempt to measure the amounts. Until these steps were taken, investigators could not begin to consider the volcanological implications of their assays.

The 40+-year-long near hiatus in eruptive activity at Halema'uma'u Crater, from 1924 until the beginning of modern chemical analysis in the 1960s, provided the time needed for instrumental analytical techniques to catch up with the evolution of conceptual models attempting to describe how volcanoes like Kīlauea work. Thermodynamic inferences of the evolving conceptual models—for example, speculations about what might be happening to gas emissions when magma moves—became better informed by improvements in gas-analysis methods.

The newly refined gas analyses could reasonably be considered the equivalent of high-quality chemical portrait photographs taken essentially instantaneously in space and time. Analogously, the regularly collected COSPEC and FLYSPEC  $\text{SO}_2$  measurements could be symbolized as time-lapse chemical photography, albeit for just a single species. These time-series gas data consequently signaled a major step at HVO toward a dynamic interpretation of volcanic processes, using geochemical data in what had formerly been solely a geophysical framework. The potential interpretative power of merging geophysical and geochemical data streams was evident. The addition of gas-geochemical time-series



**Figure 16.** Summit  $\text{SO}_2$  emission rates increased sharply through January and February 2008, while fumarole molecular C/S took on a Gerlach and Graeber (1985) Type II eruptive gas signature. *A*, Heavy fuming occurs from vents beyond eastern part of Halema'uma'u on March 10, 2008. *B*, On March 12, a new, vigorously fuming area was noted near the base of Halema'uma'u's east wall. Over the course of the next week, heat flow through this feature increased to the point where glow could be clearly seen at night. *C*, Most summit  $\text{SO}_2$  release was focused on what became known as the Overlook vent, after its formation early on the morning of March 19.



**Figure 17.** After opening of the Overlook vent in 2008, OP-FTIR spectroscopy was routinely used to monitor summit eruptive-gas composition. *A*, Infrared energy emitted by summit lava lake surface is absorbed by  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ , and  $\text{CO}$  that are present in light path between sensor and heat source. Absorption is proportional to concentration of each gas. Photograph taken February 3, 2012. *B*, Triangle plot of the first summit OP-FTIR analyses (black dot) after the formation of the Overlook vent showed gases had molecular C/S similar to those of East Rift Zone eruption (red square; an average of about 2,000 individual analyses), albeit more water-rich. Notably, this Type II, reservoir-equilibrated gas differed significantly from the Type I gases detected by T.A. Jaggar, Jr., for the lava lake that had persisted throughout the 19th century (blue diamond).



data notwithstanding, the ability to make sense of the geophysical and geochemical changes that began subtly in 2003 owes its success, in good measure, to observatory-style collection of the right volcanic-gas-studies database elements years earlier—"observatory-style" in this context meaning study of the volcano in a broad and integrated sense scientifically, spatially, and temporally.

From the conceptual models of Eaton and Murata (1960) and M.P. Ryan and colleagues (Ryan and others, 1981; Ryan, 1987), which constrained Kīlauea's plumbing and, later, its volatile-release characteristics (Gerlach and Graeber, 1985), establishment and maintenance of a record of summit  $\text{CO}_2$  emission rates to track magma supply made sense. Simultaneously, another dataset measuring East Rift Zone  $\text{SO}_2$  emission rates could be used to track the eruption rate. These measurements, together with the long-term monitoring of deformation and seismic signals, proved to be a good sentinel for the eruptive changes that occurred in the mid-2000s. Additionally, the 20+ years of carefully recorded summit  $\text{SO}_2$  emission-rate measurements, along with more than 30 years of regular sampling of Kīlauea's summit fumaroles for their molecular C/S ratios, captured the 2007–08 transition of summit gas release from passive magma-chamber degassing to active eruptive degassing.

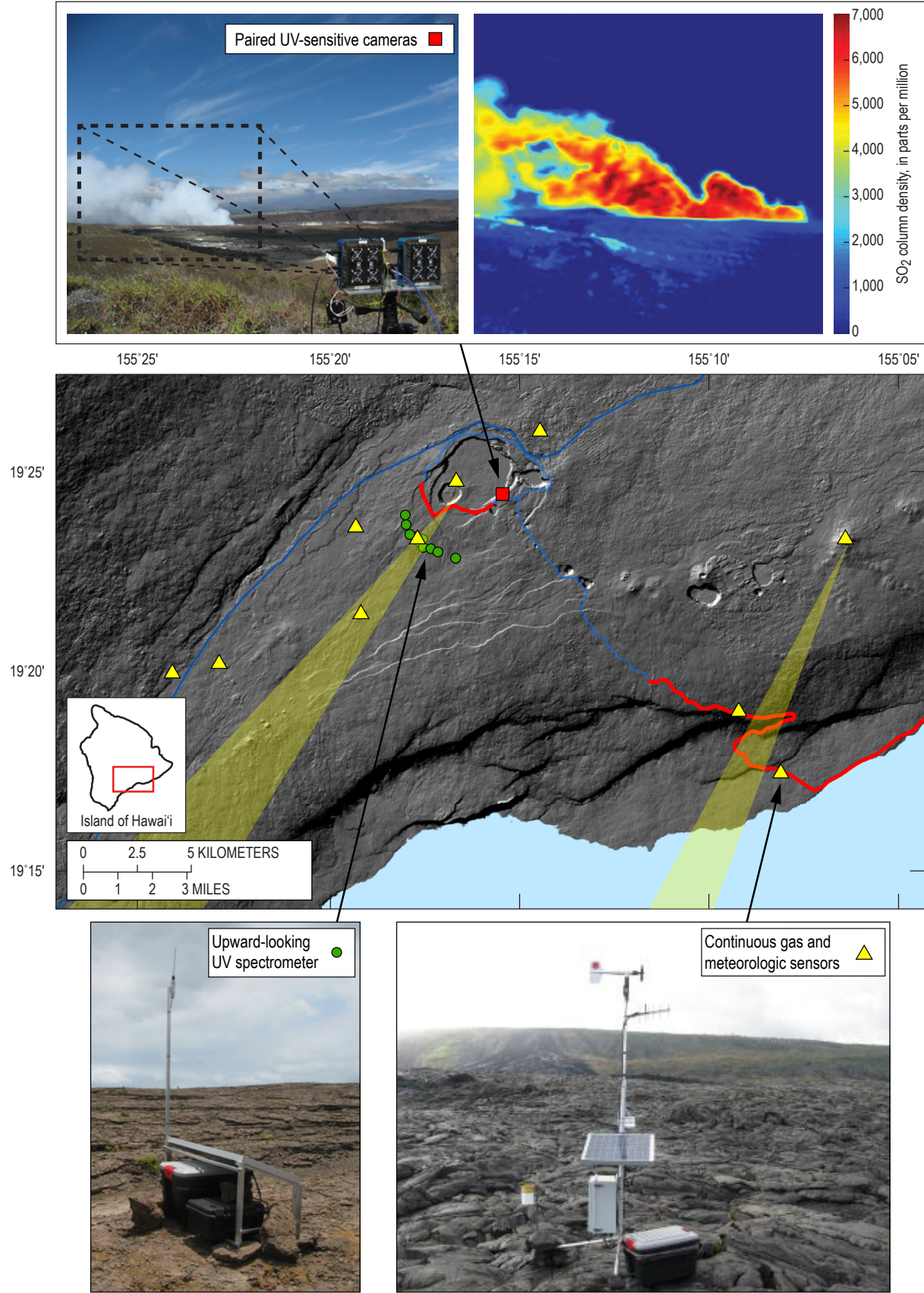
The  $\text{CO}_2$  and  $\text{SO}_2$  emission-rate records and the long-term study of fumarole chemistry began in response to the stimulation provided by a reasoned and persuasive conceptual plumbing and volatile-release model. As obvious as all this seems, however, we note that in the early 1980s, when Ryan and others' model was formulated and interpreted through Gerlach and Graeber's volatile budget lens, it was unclear precisely how it could be tested operationally and refined. Moreover, practical technology to do the testing did not yet exist.

The eruptive restlessness at Kīlauea that began with an increase in magma supply in 2003 and continued through the formation of the summit eruptive vent in 2008 persists as of this writing (September 2014). Models constructed during the 1960s through the 1980s dealt with scenarios that included either a summit or rift-zone eruption. These degassing models, however, did not speculate what might happen if both summit and rift zone eruptions occurred simultaneously. Kīlauea's eruptive activity since 2008 has, among other things, given us the opportunity to extend Gerlach and Graeber's (1985) model that predicted degassing of either a summit-reservoir-equilibrated magma or a deeper, more primitive magma. Preliminary data from 2012 indicate that (1) summit and rift zone gas  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_2$  emissions are compositionally similar—a condition not seen before; and (2) the molecular C/S ratio is not indicative of either a reservoir-equilibrated melt or a primitive magma, but rather a composition between these two end members. These two observations are consistent with a summit magma storage complex that at times is intimately connected with both the East Rift Zone eruption site and the actively convecting lava lake within Halema'uma'u Crater.

The simultaneous summit and rift zone activity that has provided an opportunity to test and refine earlier conceptual models of how Kīlauea works has also helped HVO improve its understanding of gas emissions as a volcanic hazard. The opening of the summit eruptive vent in 2008 substantially increased Kīlauea's volatile output, at least doubling the  $\text{SO}_2$  emission rate during 2008, relative to the annual average of the previous 10 years. The proximity of the new summit emission source at Halema'uma'u to downwind communities exacerbated the detrimental effects on those communities, as well as on agriculture, ecosystems, and infrastructure. Among these effects was a marked increase in the rate of exceedance of air-quality standards on the island, and the proclamation of a Federal disaster designation for Hawai'i County in mid-2008 because of gas-induced agricultural losses.

One way that gas hazard assessments were improved in response to the new eruptive activity was through a collaborative project between HVO and the University of Hawai'i to develop a vog-forecast model. Functionally, the Vog Measurement and Prediction (VMAP) project provides island residents and community officials with projections of gas and acidic-aerosol-particle exposure as much as three days in advance, so that appropriate steps can be taken to mitigate risk (Businger and others, 2011). Visitors to VMAP's Web site (<http://mkwc.ifa.hawaii.edu/vmap/index.cgi>) find a dynamic vog-forecast map with links to the Hawai'i State Department of Health's real-time  $\text{SO}_2$  and aerosol-particle data, as well as answers to frequently asked questions about vog.

**Figure 18.** Network of ground-based gas measurement stations on Kīlauea Volcano. Yellow areas on map show idealized plumes emanating from eruptive vents at summit and along East Rift Zone during normal trade-wind conditions. Blue lines, roads, with red sections denoting transects used to measure summit and East Rift Zone  $\text{SO}_2$  and  $\text{CO}_2$  emissions. Red square, temporary location of ultraviolet-light-sensitive camera system optimized to measure  $\text{SO}_2$  and trained on Kīlauea's summit eruptive plume. Top left photograph of ultraviolet (UV) camera system, and upper right image (with warm colors indicating increased  $\text{SO}_2$  concentrations), false-color photographic frame, taken on September 23, 2011. Lower left photograph, 1 in network of 10 upward-looking UV spectrometers (green circles), positioned downwind of Kīlauea's summit eruption site, measures  $\text{SO}_2$  emissions nominally every 10 seconds in real time during daylight hours. Lower right photograph, one in a network of continuous species-selective sensors (yellow triangles) measures gas concentrations and meteorological parameters every 10 minutes, telemetering data to HVO, where they are merged with emission-rate data and geophysical observations for real-time visualization of volcanic activity.





Thomas A. Jaggar, Jr.'s, provocative vision of a human presence to continuously observe active volcanism from the brink of Kīlauea Caldera has served the volcanological and residential communities well, not just in Hawai'i but worldwide. At HVO, volcanic gas studies have evolved considerably over the first hundred years of HVO's existence. We now have a good understanding of volcanic gas in terms of "what's in it." As we begin the next hundred years of volcanic gas studies, we are more likely to be asking process-related questions, like "What do the near-real-time changes we're measuring in species W and X tell us about conditions at depth Y in light of the contemporaneous tilt, seismic, and lava level data?" What we have already learned from the process side about gases has us probing hazards issues, as well, leading to such real-time questions as "What might be the implications of observed changes in species W and X for people, agriculture, and infrastructure located Z km downwind of gas-release points?"

The future of volcanic gas studies in Hawai'i is bright. HVO and its collaborators have already begun transitioning from vehicle-based SO<sub>2</sub>-emission-rate measurements to using the recently installed array of upward-looking spectrometers designed to continuously measure the SO<sub>2</sub> emitted from the summit eruptive vent during daylight hours (green circles, fig. 18). Concurrently, a newly established network of continuous gas monitors distributed from near-vent to >60 km distant measures and transmits the downwind SO<sub>2</sub> concentrations to HVO (yellow triangles, fig. 18). These data can be visualized in real time, along with geophysical and geologic data. With colleagues at CVO, HVO is testing the utility of an environmentally hardened SO<sub>2</sub>-imaging camera system that operates continuously, producing streaming video of plume-gas emissions from Kīlauea's summit during daylight hours (red square, fig. 18; Kern and others, 2013). Refinements to CO<sub>2</sub> measurement technology are extending the useful life of these sensors under rough field conditions, thus improving the quality of in situ molecular C/S ratios. These and other improvements will enhance our ability to detect changes in volcanic processes within the summit magma storage complex.

Just as fuel, air, and heat combine to make a fire, so the timing of eruptive activity, unwavering human curiosity, and an explosive growth of technology have combined to address the persistent question of how volcanoes, like those in Hawai'i, work.

## Acknowledgments

The opportunity to review a century of progress in any field provides a potent historical perspective on the subject. In relation to Hawaiian volcanic gas studies, this study has, for the authors, cultivated a deep respect for generations of workers through the years who struggled to keep telling the story, both accurately and in a way that would allow the

data of their own era to be directly comparable with those obtained before and after. Accordingly, over the past 20 years, we gratefully acknowledge the many hours of hard work contributed by USGS volunteers. We also thank Ben Gaddis, Ken McGee, and Barry Stokes of the USGS for their help with compiling the unwritten history, and Shaun Hardy of the Carnegie Institution's Geophysical Laboratory library for photoarchival assistance. The publication process was greatly facilitated by our encouraging and supportive editors, and the manuscript benefited from helpful reviews by Tom Casadevall and Lopaka Lee.

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